An investigation of substituent effects in some aromatic compounds

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A thesis entitled

AN INVESTIGATION OF SUBSTITUENT EFFECTS IN SOME AROMATIC COMPOUNDS

submitted by

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1968

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ABSTRACT

A review has been given of molecular orbital theory and of its application to calculations of ground and excited state properties of substituted aromatic hydrocarbons.

The nitrations of ortho, meta and para-xylenes and naphthalene have been studied, alone and in competitive reactions with benzene, using nitric acid/acetic acid as the nitrating medium. Partial rate factors have been determined relative to benzene.

Competitive nitrations have been carried out between: naphthalene and 2-fluoro-6-methylnaphthalene, naphthalene and 2-acetamido-6-methylnaphthalene, 2-methylnaphthalene and 2,6-dimethylnaphthalene, 2-methoxy-6-methylnaphthalene and 2,6-dimethylnaphthalene. Partial rate factors have been determined relative to naphthalene.

Proton magnetic resonance studies at 60, 100 and 220 Mc/s have been made of a series of 2,6-disubstituted naphthalenes.

An attempt has been made to interpret the experimental data by detailed Pariser-Parr-Pople self-consistent field molecular orbital calculations.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out under the supervision of Dr. D. T. Clark, and I wish to record my appreciation of his help and encouragement throughout. I would also like to express my gratitude to Dr. J. W. Emsley for invaluable assistance with the recording and interpretation of high resolution nmr spectra, Mr. R. Coult for help with glc work, and the many technical and laboratory staff for their help and co-operation. I would also like to thank Professor W. K. R. Musgrave for his interest.

Thanks are also due to Hull Education Committee for their award of a maintenance grant, without which this work would not have been possible.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1965 and December 1968. Except where acknowledged by reference it is the original work of the author and has not been submitted in whole or in part for any other degree.

The subject matter of this thesis has formed the basis for three papers, two to be published in conjunction with Dr. D.T. Clark, and one in conjunction with Drs. D.T. Clark and J.W. Emsley.

CONTENTS

List of symbols and abbreviations

Fundamental Constants

e electronic charge

m electronic mass

c velocity of light

h Planck's constant

R gas constant

N Avogadro number

Operators

H the complete electronic Hamiltonian

H_i^c the core Hamiltonian; the terms in H which are functions of just the coordinates of electron i.

$G_{ij} = e^2/r_{ij}$, an electron repulsion term in H.

H_i a one-electron Hamiltonian- non-explicit.

F the SCF operator.

$\underline{M} = e\sum_i \underline{r}_i$, the dipole moment operator.

Wave Functions

ϕ an atomic orbital; ψ a molecular orbital.

ψ_1, ψ_2 bonding molecular orbitals.

ψ_{-1}, ψ_{-2} anti-bonding molecular orbitals.

Ψ the ground state wave function written as a single determinant.

Ψ_k^{-r} an excited state obtained from Ψ by promoting an electron from ψ_k to ψ_r.

α, β the spin functions.

$\psi_r(1)\alpha(1) \equiv \psi_r(1)$, $\psi_r(1)\beta(1) \equiv \overline{\psi}_r(1)$, molecular spin orbitals.

Integrals and matrix elements

$\int \ldots dx$, integration over the electron coordinates.

$\int \ldots d\tau \equiv \langle \ldots \rangle$, integration over the spin and space coordinates of all the electrons.

$H_{rs} \equiv \langle \Psi_r | H | \Psi_s \rangle \equiv \int \Psi_r^* H \Psi_s^* dx.$

$\langle \Psi_p \Psi_q | G | \Psi_r \Psi_s \rangle \equiv \iint \Psi_p(1) \Psi_q(2) [e^2/r_{12}] \Psi_r(1) \Psi_s(2) dx_1 dx_2$

$\gamma_{\mu\nu} = \langle \phi_\mu \phi_\nu | G | \phi_\mu \phi_\nu \rangle \equiv \langle \mu\nu | G | \mu\nu \rangle \equiv \langle \mu\nu | \mu\nu \rangle$

$S_{rs} = \langle \Psi_r | \Psi_s \rangle$, the overlap integral.

$\underline{M}_{rs} = \langle \Psi_r | \underline{M} | \Psi_s \rangle$, the transition moment.

α the Hückel coulomb integral.

β the Hückel resonance integral.

$p_{\mu\nu}$ the pi bond order between atoms μ and ν.

$p_{\mu\mu} = q_\mu$, the pi electron density at atom μ.

Other symbols

E the electron affinity.

I the ionisation potential.

f the oscillator strength. (also partial rate factor)

LCAO a linear combination of atomic orbitals.

NBMO a non-bonding molecular orbital.

Z nuclear charge.

δ_{rs} the Kronecker delta.

ϵ extinction coefficient.

λ wavelength (A).

υ frequency (cm^{-1}).

INTRODUCTION

The study of substituent effects on the electronic structure and reactivity of organic compounds has occupied the attention of chemists for many years. From the study of electrophilic aromatic substitution in particular, a considerable amount of experimental data has been collected for the construction and testing of theories of substituent effects in organic molecules. Current theories of substituent effects however, have been based in the main on information derived from studies of benzene derivatives, while relatively little work has been done on substituted polycyclic aromatic compounds.

A vast amount of experimental data has been tabulated using Hammett (σ-ρ) linear free energy relationships[1], in which, for a given type of reaction, the effect of a substituent is given by a substituent constant (σ). Much of this work has been devoted to qualitative discussions of the magnitude and sign of σ for a given substituent in terms of inductive and mesomeric effects. More recently, Dewar and Grisdale[2] have attempted a more quantitative treatment with extension to naphthalene systems, but it remained dependent on several empirical parameters.

The chief drawback to the above investigations is the fact that the observed effect of a substituent depends not only on the electronic effect of the latter upon the ground state of the molecule, but also on its effect on the

transition state for the reaction under consideration.

In recent years, the development of nuclear magnetic resonance and photoelectron spectroscopy has enabled substituent effects of molecules to be studied in their ground states. Here again, very little work has been done on substituted aromatic hydrocarbons other than benzene, and this applies to both theoretical and experimental investigations.

As far as quantitative evaluations of substituent effects are concerned, the most important investigations have been based on the analysis of the electronic spectra of substituted benzenes and azulenes. The inductive and mesomeric parameters for each substituent derived from these analyses, have been incorporated into theoretical treatments based on the localised orbital model, by Murrell et al.[3] and Craig et al.[4] These investigations have concentrated on the effect of substituents on the electronic spectra. The most recent development has been the introduction of the inductive substituent parameters into standard Pariser-Parr-Pople SCF MO calculations.[5] The results of this type of treatment were very encouraging, the properties investigated being dipole moments, ^{1}H and ^{13}C chemical shifts and electronic spectra.

It is clear from this discussion that there is a lack of experimental information on the effect of substituents

on the reactivities, and ground and excited state properties of polycyclic aromatic hydrocarbons. The work described in this thesis has been planned with this in mind.

Substituent effects have been investigated from measurements of ^1H chemical shifts and from partial rate factors derived from competitive nitration reactions. Proton magnetic resonance studies at 60, 100 and 220 Mc/s have been made of 2,6-disubstituted naphthalenes, and partial rate factors have been measured for a series in which one of the substituents was methyl and the other was H, CH_3, OCH_3, F and $NHCOCH_3$. During this work, it was found that results were lacking for the partial rate factors of the xylenes with reference to nitration reactions. As these results were necessary to make comparisons between methylnaphthalenes and the corresponding benzene derivatives, partial rate factors have been determined for the xylenes.

An attempt has been made to interpret the experimental data by detailed Pariser-Parr-Pople SCF MO calculations.

Chapter 1

Substituent Effects

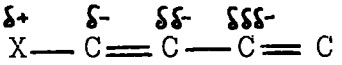
The main feature of aromatic substitution is the influence exerted by substituents on the position at which reaction occurs. Ingold[6] accounted qualitatively for positions of substitution and relative reactivities in terms of polar effects of substituents. The processes by which a substituent can affect a reaction are as follows:

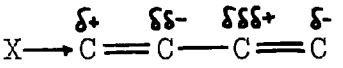
1) The σ-Inductive Effect[6] (I_σ)

This originates in the unequal sharing of the electron pair forming a covalent bond and can be transmitted to the reaction centre by successive polarisation of intervening σ bonds. It explains the increase in dipole moment along a homologous series and the increase in acidity of carboxylic acids with the introduction of halogen atoms. The effect falls off rapidly and smoothly as the distance from the substituent increases.

2) The pi-Inductive Effect[7] (I_π)

The charge produced at a conjugated atom adjacent to the substituent may polarise the corresponding pi electron system. This effect explains the difference between ground and excited state measurements of the inductive and mesomeric effects of the halogens.[7] The I_π effect produces a long range polarisation similar to the mesomeric effect (see below), but the latter changes the electron densities only at alternate atoms, while the former builds up charge on one set of atoms and decreases it on the other.[7,8]

$+I_\sigma$ 

$+I_\pi$ 

3) The Mesomeric Effect[6] (M)

The pi electron system can be polarised by resonance interaction with the substituent. An electron-releasing substituent (+M) will act as follows:

+M 

As with the I_π effect, due to delocalisation of electrons, the mesomeric effect is transmitted over a long range.

4) The Field Effect

The electric dipole field of the substituent may influence the reaction centre directly across space. It is not easy to distinguish between this effect and inductive effects but Dewar et al.[2] have shown that it can be significant.

5) Hyperconjugation

A further effect which cannot be entirely discounted is hyperconjugation. This is the process by which a group such as an alkyl group can conjugate with an aromatic system as though it possesses electrons of pi symmetry. Theoretical studies[9,10] show that a conjugative mode of electron release

by alkyl groups is feasible, and spectroscopic evidence is also in favour of a methyl group behaving as a +M substituent.

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There are two approaches for the interpretation of substituent effects in organic chemistry. The first is based on the Hammett linear free energy relationship and can be discussed in terms of Ingold's definitions of inductive and mesomeric effects. The second approach is based on evaluation of substituent effects from electronic spectroscopy and requires more careful definitions in quantum mechanical terms.

a) Linear Free Energy Relationships

The reactivities of functional centres in the side-chains of aromatic compounds are correlated very well by the Hammett linear free energy relationship:[1]

$$\log k_X/k_O = \sigma_X \rho_Y \qquad (1)$$

in which k_X and k_O are equilibrium or rate constants for the substituted and unsubstituted compounds, respectively, σ_X is a constant of the substituent x and ρ_Y is a constant of the reaction at some centre y.

The validity of equation (1) is restricted to substituents in the meta- and para-positions of the benzene ring, and the effect of a substituent will depend on its mutual orientation with the reaction centre. Thus, two different substituent constants, σ_m and σ_p are required for meta- and para-substitution, respectively.

The form of the Hammett equation requires that there be no mutual conjugation between the reaction centre and the substituent, otherwise substituents will require special σ values when conjugation is possible.

When the Hammett equation is applied to aromatic substitution, resonance interactions between the substituent and the reaction centre are much greater than in side-chain reactions. Brown et al.[11] proposed that a new substituent constant, σ^+, should be used for

these reactions, σ^+ differing from σ by an amount depending on the resonance interaction between the substituent and the aromatic nucleus in the transition state. Since σ^+ depends in part on the above resonance interaction, it should depend on the extent of formation of the new σ-bond in the transition state. The latter is dependent on the nature of the reagent, increasing with ρ[12]. Acccordingly, Knowles et al.[13] proposed a further modification to take this into account:

$$\log k/k_o = \rho(\sigma_G + \sigma_R) \qquad (2)$$

For a very reactive reagent, the transition state will resemble the ground state of the molecule and the reaction rate will be governed by ground state electron densities. σ_G represents the polarisation of the reaction centre in the ground state. For less reactive reagents, the σ-bond will be appreciably formed at the transition state and a resonance interaction (σ_R) will be more important than σ_G. σ_R will increase with ρ and a linear relationship:

$$\sigma_R = \sigma_P\rho \qquad (3)$$

was suggested[13], where σ_P is the ability of the substituent to supply electrons to the reagent by resonance interaction. Thus, equation (2) becomes:

$$\log k/k_o = \sigma_G^{-G-} + \sigma_P\rho^2 \qquad (4)$$

This is similar to the equation proposed by Yukawa and Tsuno:[14]

$$\log k/k_o = \sigma\rho + \sigma'\rho' \qquad (5)$$

where ρ' is a new constant measuring the sensitivity of the reaction centre to mutual conjugation, and σ' is a corresponding measure of the conjugative power of the substituent.

Both of these equations have been used successfully, but they suffer the same deficiency of the Hammett equation, namely the excess of empirical parameters.

b) The Derivation of Substituent Constants from Electronic Spectra

A satisfactory theory of substituent effects requires a quantitative scale such as that given by Hammett σ-ρ values, defined with reference to the electronic properties of the substituent. Electronic spectrocopy provides a good basis for constructing a quantitative theory, because changes in energy brought about by substituents can be observed directly. The only limitation is that differences in energy between ground and excited states, and not absolute energies, are observed. In addition, only the energy-change of the pi-electrons is observed. However, the pi-electrons are mainly responsible for the characteristic properties of aromatic compounds, and these properties should be predictable by calculating substituent effects on the pi-electrons.

It is usual to describe substituent effects on the electron distribution in a molecule in terms of the inductive and mesomeric effects, which were originally defined (see above) by Ingold[6] by reference to the classical theory of valence. In quantum mechanics, however, more exact mathematical definitions are necessary.

The pi-inductive effect of a substituent is defined[15] as the effect of its potential field on the pi-electrons of the

unsubstituted molecule.

The mesomeric effect of a substituent is defined as its ability to extend the space over which the pi-electrons of the molecule are delocalised.

These effects can be treated separately if the mixing of states (or orbitals) can be adequately described by first order perturbation theory, and the energy changes by second order perturbation theory.

Considering a substituted ethylene: if ψ_1 and ψ_{-1} are the bonding and anti-bonding pi orbitals of ethylene, and the substituent X possesses an orbital ψ_s of pi-symmetry, then the orbitals of the substituted molecule can be written:

$$\psi = c_1\psi_1 + c_{-1}\psi_{-1} + c_s\psi_s \qquad (6)$$

Under the influence of the inductive perturbation, I, ψ_1 mixes with ψ_{-1}, and the mesomeric perturbation, M, mixes ψ_1 and ψ_{-1} with ψ_s, the first-order approximation to the bonding orbital being:

$$\psi^* = \psi_1 + \frac{\langle\psi_1|H^*|\psi_{-1}\rangle}{\epsilon_1 - \epsilon_{-1}}\psi_{-1} + \frac{\langle\psi_1|H^*|\psi_s\rangle}{\epsilon_1 - \epsilon_s}\psi_s \qquad (7)$$

where $H^* = H + I + M$. H is the unperturbed Hamiltonian.

To this order, the extent to which ψ_{-1} mixes with ψ_1 is independent of the mesomeric perturbation elements $\langle\psi_1|H^*|\psi_s\rangle$ and $\langle\psi_{-1}|H^*|\psi_s\rangle$, and the extent to which ψ_s mixes with ψ_1 is independent of the inductive perturbation element $\langle\psi_1|H^*|\psi_{-1}\rangle$.

The influence of the substituent on the energies of ψ_1 and ψ_{-1} can be calculated by second order perturbation theory as:

$$E_1^* = E_1 + \langle\psi_1|I|\psi_1\rangle + \langle\psi_1|M|\psi_1\rangle + \frac{\langle\psi_1|M|\psi_s\rangle^2}{E_1 - E_s} + \frac{\langle\psi_1|I|\psi_{-1}\rangle^2}{E_1 - E_{-1}} \quad (8)$$

$$E_{-1}^* = E_{-1} + \langle\psi_{-1}|I|\psi_{-1}\rangle + \langle\psi_{-1}|M|\psi_{-1}\rangle + \frac{\langle\psi_{-1}|M|\psi_s\rangle^2}{E_1 - E_s} + \frac{\langle\psi_1|I|\psi_1\rangle^2}{E_{-1} - E_1} \quad (9)$$

$$E = E_{-1}^* - E_1^*$$

$$= [\langle\psi_{-1}|I|\psi_{-1}\rangle - \langle\psi_1|I|\psi_1\rangle + \frac{\langle\psi_{-1}|I|\psi_1\rangle^2}{E_{-1} - E_1} + \frac{\langle\psi_1|I|\psi_{-1}\rangle^2}{E_{-1} - E_1}$$

$$+ [\langle\psi_{-1}|M|\psi_{-1}\rangle - \langle\psi_1|M|\psi_1\rangle + \frac{\langle\psi_{-1}|M|\psi_s\rangle^2}{E_{-1} - E_s} + \frac{\langle\psi_1|M|\psi_s\rangle^2}{E_s - E_1} \quad (10)$$

In an alternant hydrocarbon, within the zero-overlap approximation, the ground and excited states have the same, uniform, charge density[16]. Now integrals like $\langle\psi_1|I|\psi_1\rangle$ represent the interaction of electrons in a state ψ_1 with I, and for alternant hydrocarbons will equal $\langle\psi_{-1}|I|\psi_{-1}\rangle$. Hence, to first order:

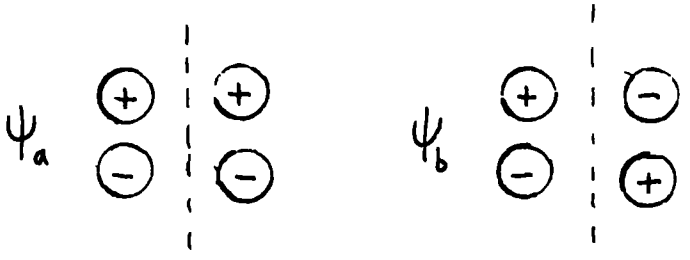
$$E_{-1}^* - E_1^* = [\langle\psi_{-1}|I|\psi_{-1}\rangle - \langle\psi_1|I|\psi_1\rangle] + [\langle\psi_{-1}|M|\psi_{-1}\rangle - \langle\psi_1|M|\psi_1\rangle]$$

$= 0$, for alternant hydrocarbons. (11)

That is, the first order change in the transition energy is zero.

In a non-alternant hydrocarbon, there is a pi-electron density change on excitation and therefore a corresponding first order inductive shift. If it is a valid assumption that the shifts in the 5000 Å azulene band are dominated by the inductive shift, an analysis of the shifts will give values of the pi-inductive parameter, α'. ($\alpha' = \langle \phi_\mu | V | \phi_\mu \rangle$, where μ is the substituted C atom, V is the potential field of the substituent, and α' is the change in the Coulomb integral of the substituted C atom, as defined by Hückel theory). To first order, the shifts are proportional to α' multiplied by the electron density change on excitation at the substituted C atom.

A second estimation of α' can be made from the second order inductive shift in alternant hydrocarbons. This is rather sensitive to the relative positions of substituents. For example, consider two states of ethylene, one (a) totally symmetric and one (b) which is antisymmetric to a perpendicular reflection plane.



For ψ_a to mix with ψ_b, the perturbation must have a component with the same symmetry as the product $\psi_a \psi_b$, which is antisymmetric with respect to the reflection plane. The perturbing field arising from mono-substitution has such a component, but those from cis- and trans-di-substituted ethylenes have not, and there will be no inductive shift. For gem-disubstitution, the perturbation is antisymmetric and must be twice as large as for the mono-substituted ethylene. Since the second order energy changes depend on the square of the perturbation, the energy shifts for gem-disubstitution will be four times the shifts for mono-substitution. Hence the second order inductive shift = $I_n \alpha'^2$, where I_n depends on the number and relative positions of the substituents.

Table 1 shows the frequency shift of the 2600 Å band of benzene for substituents that are almost solely inductive (aza N and F), and those which have a mesomeric effect as well (Cl and CH_3). The Cl and CH_3 spectra show that the frequency shift depends on the number of substituents and not on their relative positions, while for F and (N) the reverse is true. By separating the observed frequency shifts into a part which is additive in substituents and a part which is not, it is possible to deduce the magnitudes of the inductive and mesomeric effects.[17]

TABLE 1

Frequency shifts(cm^{-1}) in the 2600Å band of benzene.[18]

Position of substitution	(N)	F	Cl	CH_3
1	-400	270	1030	610
1,2	-1250		1850	920
1,3	-1800	200	1900	1150
1,4	900	1290	2340	1390
1,2,3			2600	1260
1,2,4		950	3000	1570
1,3,5	-5600	-440	2600	1520
1,2,3,4			3550	1700
1,2,3,5			3450	1750
1,2,4,5	-300	1480	3850	1890
1,2,3,4,5			4250	2030

The frequency shifts in the visible band of azulene and the 2850Å band of naphthalene arising from methyl and phenyl substitution are shown in table 2. Here, CH_3 exerts a first order inductive shift in azulene, in naphthalene a second order shift. Azulene is the most extensively studied of the non-alternants. It has been shown by Plattner[19] that the frequency shift of the first azulene band follows an additivity rule, and therefore the second order inductive shift is small. The phenyl group

has a relatively small effect on the azulene band although it can have a large mesomeric effect. Hence, for substituents with weak mesomeric effects, the shifts in the azulene band can be attributed almost entirely to the inductive effect, and even for strongly mesomeric substituents the average mesomeric effect over all positions of substitution may be small.

TABLE 2

Frequency shifts(cm^{-1}) for azulene and naphthalene.[18]

Position of substitution	Azulene				
	1	2	4	5	6
CH_3	+790	-430	-370	+350	-460
C_6H_5	+765	-50	+170	+405	+330

Position of substitution	Naphthalene	
	1	2
CH_3	+800	+100
C_6H_5	+1600	+1300

The second order inductive shift of the benzene 2600Å band has been analysed in detail by Murrell and McEwen[20]. The overall shift can be represented by the relationship:

$$E = nA + I_n\alpha'^2 \qquad (12)$$

where n is the number of substituents, $I_n\alpha'^2$ is the second order inductive shift as above, and A contains all

additive contributions to the shift, i.e. first order inductive, mesomeric and zero-point vibration energy changes. A graph of $\frac{E}{n}$ versus $\frac{I_n}{n}$ should give a straight line with slope α'. Values of α' estimated in this way are given in table 3.

TABLE 3

Calculated values of α'.[18]

Substituent	1-Azulene (cm^{-1})	Benzene (cm^{-1})
F		+8780
Cl	+3540	+5370
Br	+2960	+5480
CH_3	+3290	+4290
$CH_2.CH_3$	+3630	+4610
$CH.(CH_3)_2$	+3300	+3840
$C(CH_3)_3$		+3000
CF_3		-3950
CN	-3300	-6710
COOH	-4750	-11850
CHO	-5420	-17280
NO_2	-8710	
OH		+13780
OMe		+11870
NH_2	+13750	+13880
(N)	-18750	-17500

From the spectra of homosubstituted benzenes, one can deduce the magnitude but not the sign of α'. Aza nitrogen is certainly pi-electron attracting relative to carbon, so that α' is negative for this substituent.

The values of α' deduced from the azulene and benzene spectra are in reasonable agreement, except for those substituents (CHO, COOH, CN) which have strong -M effects. These substituents produce a hypsochromic shift at the 1-

position of azulene, and if the mesomeric effect is producing a bathochromic shift, which is the expected behaviour, then α' will be underestimated.

The inductive effect of a substituent on the σ electrons (I_σ) of an aromatic hydrocarbon is not usually the same as that on the pi-electrons (I_π), e.g. the halogens have I_π positive and I_σ negative. It has been shown that the disagreement in the literature on the relative mesomeric and inductive strengths of the halogens is due to non-recognisance of this fact.[7] In the σ-bond, fluorine is electron-attracting because of the lower potential well at that nucleus compared with carbon. However, the fluorine $2p_z$ orbital contains two electrons, so that an electron in an adjacent carbon $2p_z$ orbital experiences a pi-electron repulsion. (partly electrostatic and partly due to the Pauli exclusion principle). This is taken into account by a reduction in the coulomb integral at that C atom.

In a localised-orbital model, the mesomeric effect is introduced by allowing the ground and locally excited states to interact with charge-transfer states. The ground state can be represented by X-R and the locally excited state by $X\text{-}R^*$. If there is some overlap between the sub-stituent and hydrocarbon pi-orbitals, then both these states interact with the charge-transfer states $X^+\text{-}R^-$ and $X\text{-}R^+$. For every substituent there is a set of charge-

transfer states, and it has been shown[17,20] by second order perturbation theory that each set has an independent effect on the hydrocarbon states. Within this approximation the mesomeric effects of substituents are additive. From that part of the substituent shift which is proportional to the number of substituents introduced, the parameter A is derived in equation (12). This has been tabulated for a number of substituents by Petruska.[21]

The order of the mesomeric strengths of the halogens is roughly that expected from their relative ionisation potentials: F<Cl<Br<I, but is the reverse of the order predicted from ground state properties.[7] From a property of the ground state which is correlated with electron density in the ring, it is not possible to separate a $+I_\pi$ and a +M effect, since both effects build up charge at the o- and p-positions, although the charge at the m-position is decreased slightly by the former.[8] The meso--meric effect is usually estimated from ground state properties as a combination of I_π + M.

CHAPTER 2

Molecular Orbital Theory and Electronic Spectra.

Simple Molecular Orbital Theory

The molecular orbital (MO) theory of the electronic structure of molecules is the natural extension of the atomic orbital theory of atomic structure to molecules. Each electron in a molecule is described by a wave function ψ, which is called a molecular orbital.

The energies E, of the MO 's are obtained from the Schrodinger equation

$$H\psi = E\psi \tag{13}$$

where H is the Hamiltonian operator.

For a single particle of mass m (in this case an electron) moving in a potential field V, the Hamiltonian excluding spin is:

$$H = -\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V \tag{14}$$

For a system of nuclei ($\mu, \upsilon \ldots$) and electrons (i, j...) the Hamiltonian is:

$$H = -\sum_{\mu}\frac{h^2}{8\pi^2 M_\mu}\nabla^2_{\nu_\mu} - \sum_{i}\frac{h^2}{8\pi^2 m}\nabla^2_{i} + \sum_{ij}\frac{e^2}{r_{ij}} + \sum_{\mu\upsilon}\frac{Z_\mu Z_\upsilon}{r_{\mu\upsilon}}e^2 - \sum_{\mu i}\frac{Z_\mu e^2}{r_{\mu i}} \tag{15}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The first two terms are the kinetic energy operators of the nuclei and electrons respectively. The third term is the mutual potential energy of repulsion of the electrons, ($\sum_{ij}$ means a sum over all pairs of electrons) r_{ij} being the distance between electrons i and j. The fourth term is the repulsion energy of the nuclei, (Ze is the nuclear charge), and the last term the potential energy of attraction between the electrons and the nuclei.

Using the Born-Oppenheimer approximation, the total wave function can be separated into an electronic and a nuclear part. The electronic wave function is obtained for fixed positions of the nuclei by neglecting the first term in the Hamiltonian. Any future reference to the total wave function, energy or Hamiltonian will mean the electronic terms only.

Because of the many variables present, such a Hamiltonian cannot normally be used and it is necessary to use an approximate operator in the Schrodinger equation. In the empirical MO theory, a simple form for the Hamiltonian is used. (e.g. in Huckel theory it is given in non-explicit form.)

Using the Schrodinger equation, the energies of the MO 's can be calculated, and the ground state of the molecule constructed by allocating the available electrons to the MO 's of lowest energy, subject to the restriction imposed by the Pauli exclusion principle. The total wave

function (Ψ) is taken as a product of the ψ's of all the electrons considered. An excited state is produced by raising an electron from a filled orbital to a vacant orbital and, in the simple approach, the difference between the two levels is the excitation energy.

There are two deficiencies of this approach:

a) The Pauli exclusion principle is not adequately taken into account, since no spin wave functions are incorporated and so exert no influence on the energy levels. As a result, an excited state in which two electrons are unpaired will have the same energy whether it be a singlet or a triplet state.

b) Every MO is constructed as if other electrons were absent, neglecting the mutual repulsion between electrons. Therefore to improve the method, electron spin must be taken into account and the Hamiltonian must be made more explicit by including more interactions between the charged particles which make up a given system.

2. Antisymmetrisation of Molecular Orbitals

A spin function α or β can be associated with each space function MO to give Molecular Spin Orbitals (MSO). For example, we can have $1s\alpha$ or $1s\beta$ as the complete wave function of an electron in a 1s orbital. For brevity these may be written 1s and $\overline{1s}$ if no confusion with a simple orbital function can arise. A wave function for a many-

electron system might be written as:

$$\psi_a(1)\,\bar{\psi}_a(2)\,\psi_b(3)\,\ldots\,\bar{\psi}_k(n) \qquad (16)$$

but an equally good function could be:

$$\psi_a(2)\,\bar{\psi}_a(1)\,\psi_b(3)\,\ldots\,\bar{\psi}_k(n) \qquad (17)$$

or any other of the n! functions which can be obtained by promoting the n electrons amongst these spin orbitals. The most general wave function will be some combination of these n! functions. The correct combination is determined by the fact that an acceptable wave function must change sign on exchanging any two electrons. For two electrons, the function:

$$\frac{1}{2^{\frac{1}{2}}}\left[\,\psi_a(1)\bar{\psi}_a(2) - \psi_a(2)\bar{\psi}_a(1)\,\right] \qquad (18)$$

satisfies this condition. In general, a determinant of the form:

$$\frac{1}{n!^{\frac{1}{2}}}\begin{vmatrix} \psi_a(1)\,\bar{\psi}_a(1) & \ldots & \bar{\psi}_k(1) \\ \psi_a(2)\,\bar{\psi}_a(2) & \ldots & \bar{\psi}_k(2) \\ \ldots & \ldots & \ldots \\ \psi_a(n)\,\bar{\psi}_a(n) & \ldots & \bar{\psi}_k(n) \end{vmatrix} \qquad (19)$$

satisfies the condition that it changes sign on exchanging any two electrons, since interchanging two rows of a determinant changes its sign. Such a normalised determinant is called a Slater determinant and may be abbreviated:

$$|\psi_a \bar{\psi}_a \cdots \bar{\psi}_k| \qquad (20)$$

This antisymmetric-exchange property of electronic wave functions is merely a more general statement of the Pauli exclusion principle. If two electrons have the same four quantum numbers, then they occupy the same spin orbital. The determinant will then be zero since two of its columns are identical: in other words, such a function cannot exist.

For two electrons (1 and 2) there are four space functions:

$$\alpha(1)\,\alpha(2)$$

$$\frac{1}{2^{\frac{1}{2}}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \quad \text{symmetric} \qquad (21)$$

$$\beta(1)\,\beta(2)$$

$$\frac{1}{2^{\frac{1}{2}}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad \text{asymmetric} \qquad (22)$$

The MSO 's are then:

Singlet:
$$\frac{1}{2^{\frac{1}{2}}}\left[|\psi_a \bar{\psi}_b| - |\bar{\psi}_a \psi_b|\right] \qquad (23)$$

$$|\psi_a \psi_b|$$

Triplet:
$$\frac{1}{2}\left[|\psi_a \bar{\psi}_b| + |\bar{\psi}_a \psi_b|\right] \qquad (24)$$

$$|\bar{\psi}_a \bar{\psi}_b|$$

The wave functions can be improved by taking a linear combination of Slater determinants which have different electron configurations: this is known as configurational interaction (CI).

3. The Linear Combination of Atomic Orbitals(LCAO) Approximation.

When an electron gets close to a nucleus it experiences a potential due to that nucleus which swamps the effect of the other nuclei in the molecule. It is therefore a reasonable assumption that in the regions close to the nuclei the MO 's look very like atomic orbitals(AO 's). This is the basis of the LCAO approximation to the MO 's of a molecule. Thus:

$$\psi = \sum_{\upsilon} c_{\upsilon} \phi_{\upsilon} \qquad (25)$$

where ϕ_{υ} are AO 's and the coefficients have to be determined. If a large number of AO 's is included in the expansion, it is possible to obtain good MO 's. In pi-electron theory, however, it is usual to include only one pi-orbital per atom.

4. The Huckel Approximation

Huckel[22] developed a very simple form of MO theory in which a non-explicit Hamiltonian is used. ψ is assumed to be an eigenfunction of a one-electron operator H, so that:

$$H\psi = E\psi \qquad (26)$$

Substituting for ψ in this equation, multiplying on the left by ϕ_{μ}^{*} and integrating over the spacial co-ordinates of the electrons, gives:

$$\sum_{\upsilon} c_{\upsilon}(H_{\mu\upsilon} - E S_{\mu\upsilon}) = 0 \qquad (27)$$

where $H_{\mu\upsilon} = \langle \phi_\mu^* | H | \phi_\upsilon \rangle$ (28)

$S_{\mu\upsilon} = \langle \phi_\mu^* | \phi_\upsilon \rangle$ (29)

If there are n AO 's in the expansion there will be n MO 's and n secular equations of the type(27), and these will have non-trivial solutions only if the secular determinant is zero: that is

$$| H_{\mu\upsilon} - ES_{\mu\upsilon} | = 0 \qquad (30)$$

In the LCAO approximation, the problem is deciding on the form of the one-electron Hamiltonian. The Huckel approach is to decide on the form of the matrix elements $H_{\mu\upsilon}$ and then to use the resulting orbitals without attributing any special significance to them.

In an aromatic hydrocarbon, each atom in the conjugated system contributes one AO to the MO 's, and each atom is in a similar environment. The Huckel approximations to the secular equations for the pi-electrons of these molecules are:

1) Zero-overlap is assumed even between neighbouring AO 's. i.e. $S_{\mu\upsilon} = 0$ if $\mu \neq \upsilon$. Assuming that the individual AO 's are normalised, $S_{\mu\mu} = 1$.

2) $H_{\mu\mu}$ is assumed to be the same for each atom. It is given the symbol α and is called the Coulomb integral.

3) $H_{\mu\upsilon}$ is a constant β if atom μ is bonded to υ $(\mu \rightarrow \upsilon)$. β is called the resonance integral.

4) $H_{\mu\upsilon} = 0$ if μ and υ are not bonded together.

With these approximations the secular equations become:

$$\sum_{\upsilon \to \mu} c_\upsilon \beta - c_\mu (\alpha - E) = 0 \qquad (31)$$

or by writing $x = \frac{\alpha - E}{\beta}$, they become:

$$\sum_{\upsilon \to \mu} c_\upsilon + x c_\mu = 0 \qquad (32)$$

The secular determinant now has x everywhere on the diagonal and 1 in the off-diagonal elements of row μ column υ if $\upsilon \to \mu$, but 0 otherwise. Solution of the determinant yields energy levels $\alpha \pm x\beta$ where +x refers to bonding and -x refers to anti-bonding orbitals. (β being a negative quantity).

The pi-electron distribution is described in terms of the pi-charge q_μ, at each atom:[23]

$$q_\mu = \sum_i n_i c_{\mu i}^2 \qquad (33)$$

and the pi-bond-order $p_{\mu\upsilon}$, for any pair of atoms μ and υ:[23]

$$p_{\mu\upsilon} = \sum_i n_i c_{\mu i} c_{\upsilon i} \qquad (34)$$

where n_i is the number of electrons in the ith. MO.

Coulson[24] also defined the term free valence F_μ, in terms of the bond-orders:

$$F_\mu = N_{max} - N_\mu \qquad (35)$$

where N_μ is the sum of the bond-orders between atom μ and

its neighbours, $N_{max} = 3$* being a theoretical maximum value of N derived from trimethylmethane[25].

In Hückel theory, the pi-bonding energy E is approximated as a sum of orbital energies ε, computed as if the electrons were independent. Coulson and Longuet-Higgins[8] showed that the total pi-energy in the ground state is:

$$E = \sum_{\mu} q_{\mu}\alpha + 2\sum_{\mu>\upsilon} p_{\mu\upsilon}\beta \qquad (36)$$

The introduction of a heteroatom into an unsaturated system will require new values for α and β. Changes in α and β are usually expressed in terms of α_c and β_{c-c} with benzene as the reference substance.

$$\alpha_X = \alpha_C + h_X\beta_{C-C} \qquad (37)$$

$$\beta_{C-X} = k_{C-X}\beta_{C-C} \qquad (38)$$

It is difficult to deduce definite values of h_X and k_{C-X} because Hückel parameters depend on the property being studied, though α_X must be related to the electronegativity of atom X, and it has been suggested that h_X is linearly related to the electronegativity difference of X and C.[25]

An alternative method is to consider the introduction of a heteroatom to be producing a perturbation on the MO 's and energies of the isoelectronic hydrocarbon.

From equation(36),

$$dE = \sum_{\mu} q_{\mu}\, d\alpha_{\mu} + 2\sum_{\mu>\upsilon} p_{\mu\upsilon}\, d\beta_{\mu\upsilon} + \sum_{\mu}\alpha_{\mu} dq_{\mu} + 2\sum_{\mu>\upsilon}\beta_{\mu\upsilon} dp_{\mu\upsilon} \qquad (39)$$

and $$\frac{\partial E}{\partial \alpha_\mu} = q_\mu \; ; \qquad \frac{\partial E}{\beta_{\mu\upsilon}} = 2p_{\mu\upsilon} \tag{40}$$

Hence $$\frac{\partial q_\mu}{\partial \alpha_\upsilon} = \frac{\partial^2 E}{\partial \alpha_\mu \partial \alpha_\upsilon} = \frac{\partial q_\upsilon}{\partial \alpha_\mu} = \pi_{\mu\upsilon} \tag{41}$$

That is, a change in α_μ produces the same perturbation to the pi-electron charge at atom υ as a similar change in α_υ would produce at atom μ. $\pi_{\mu\upsilon}$, which is called the mutual polarisability,[8] may also be expressed in terms of the coefficients and energies of the MO 's:

$$\pi_{\mu\upsilon} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{\mu j} c_{\mu k} c_{\upsilon j} c_{\upsilon k}}{\varepsilon_j - \varepsilon_k} \tag{42}$$

In particular the self-polarisability of atom μ is:

$$\pi_{\mu\mu} = \frac{\partial q_\mu}{\partial \alpha_\mu} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{\mu j}^2 c_{\mu k}^2}{\varepsilon_j - \varepsilon_k} \tag{43}$$

It will be shown later that the terms q_μ, F_μ, and $\pi_{\mu\mu}$ can be used as reactivity indices in a simple study of reactions.

The advantage of Hückel theory is its simplicity, but because of the neglect of electron interaction terms in the Hamiltonian its success depends on the variation of the empirical parameters α and β to suit the particular experimental conditions being studied.

5. Self-Consistent Field Equations and the Energies of Antisymmetrised Molecular Orbitals

The energy of a wave function may be calculated from the equation:

$$E = \langle \Psi H \Psi \rangle \tag{44}$$

where H is the complete electronic Hamiltonian:

$$H = \sum_i H^c(i) + \sum_{ij} \frac{1}{r_{ij}} + V_{nn} \tag{45}$$

$H^c(i)$, the core Hamiltonian, consists of the kinetic energy operator and the electron-nuclear attraction terms for electron i, and where V_{nn} is the nuclear repulsion energy.

Substituting equations(20) and(45) into(44) gives:

$$E = \langle | \psi_a \bar{\psi}_a \ldots\ldots \bar{\psi}_k | \left[\sum_i H^c(i) + \sum_{ij} \frac{1}{r_{ij}} + V_{nn} \right] | \psi_a \bar{\psi}_a \ldots . \bar{\psi}_k | \rangle \tag{46}$$

The determinant may be written in the form:

$$|\psi_a \; \bar{\psi}_a \; \ldots\ldots \; \bar{\psi}_k|$$

$$\frac{1}{\sqrt{n!}} (1 + P) \, \psi_a(1) \, \bar{\psi}_a(2) \psi_b(3) \ldots\ldots \bar{\psi}_k(n) \tag{47}$$

for a closed-shell system; where P is an operator which permutes all the electrons 1....n among the available spin orbitals and multiplies by $\pm$' (depending on whether it is an odd or even permutation), so as to preserve the asymmetry of the function. There are n! terms in the determinant on the right of equation(46), but since there

is nothing special about this particular allocation of electrons to orbitals, all of these terms must give the same contribution to E. Multiplying this one term by n! gives:

$$E = \langle (1+P)\ \psi_a(1)\overline{\psi}_a(2)\ldots\ldots\overline{\psi}_k(n)\ |H|\ \psi_a(1)\overline{\psi}_a(2)\ldots\ldots\overline{\psi}_k(n)\rangle \quad (48)$$

The Hamiltonian contains a sum of one- and two-electron operators, so that unless there is at least one term for which all but two electrons are in the same place on both sides of the operator, the matrix element will be zero because of the orthogonality of the spin orbitals. (Since for every term in the Hamiltonian $\frac{e^2}{r_{ij}}$, we can integrate over the co-ordinates of all the other electrons, and if any one electron is in a different orbital on each side of the matrix element this will give zero.) Thus after integration over the co-ordinates not involved in the operator

$$\langle\ \psi_a(1)\overline{\psi}_a(2)\ldots\ldots\overline{\psi}_k(n)\ \ |H|\ \psi_a(1)\overline{\psi}_a(2)\ldots\ldots\overline{\psi}_k(n)\ \rangle$$

becomes:

$$2\sum_{r=a}^{k} H^c_{rr} + 2\sum_{\text{pairs } rs} J_{rs} + V_{nn} \quad (49)$$

since there are two electrons associated with each MO.

$$H^c_{rr} = \langle\psi_r|H^c|\psi_r\rangle \quad (50)$$

$$J_{rs} = \langle\psi_r(i)\psi_s(j)|\tfrac{1}{r_{ij}}|\psi_r(i)\psi_s(j)\rangle \quad (51)$$

J_{rs} is called a Coulomb integral.

Consider now a term where electrons are exchanged in $\psi_a(1)$ and $\overline{\psi}_a(2)$ on the left hand side of (48). This gives the term

$$- \langle \overline{\psi}_a(1)\,\psi_a(2)\ldots\ldots\overline{\psi}_k(n) \;|H|\; \psi_a(1)\,\overline{\psi}_a(2)\ldots\ldots\overline{\psi}_k(n) \rangle \qquad (52)$$

which is zero because of the orthogonality of the spin functions. If electrons are exchanged in $\psi_a(1)$ and $\psi_b(3)$ this gives the term:

$$-K_{13} = - \langle \psi_a(1)\psi_b(3) \left| \frac{1}{r_{13}} \right| \psi_a(3)\psi_b(1) \rangle \qquad (53)$$

which is an exchange integral. There is one such term for all pairs of spin orbitals rs. If more than two electrons are exchanged there will be at least three electrons in different spin orbitals on the left and right hand sides of the operator and these terms will be zero.

The total energy of a closed shell system is thus:

$$E = 2 \sum_r H^c_{rr} + \sum_{\text{pairs rs}} 2(J_{rs} - K_{rs}) + V_{nn} \qquad (54)$$

where $$K_{rs} = \langle \psi_r(i)\psi_s(j) \left| \frac{1}{r_{ij}} \right| \psi_s(i)\psi_r(j) \rangle \qquad (55)$$

The variation principle can now be applied to the wave function(9) to find the conditions that the energy (54) be minimized. Applying the conditions is sufficient

to define the orbitals ψ , which when evaluated in this way are called self-consistent field(SCF) orbitals. The orbitals defined with respect to the antisymmetrised product(19) are called Hartree-Fock SCF antisymmetrised molecular orbitals.(ASMO)

Suppose that the function(20) does not give the lowest energy of the state. Then there is some other function

$$\psi' = |\psi_a' \psi_b \cdots\cdots \psi_K| \qquad (56)$$

which has a lower energy. Assume that the difference between ψ_a and ψ_a' is small and can be written as:

$$\psi_a' = \psi_a + c_t \psi_t \qquad (57)$$

where ψ_t is a spin orbital orthogonal to the set $\psi_a \ldots \psi_K$. ψ_a' will still be normalised, providing c_t is small, because re-normalisation will only involve a term in c_t^2 . Equation(56) can now be written:

$$\psi' = |\psi_a \psi_b \cdots\cdots \psi_K| + c_t |\psi_t \psi_b \cdots \psi_K| \qquad (58)$$

$$= \psi + c_t \psi_a^t \text{ (say)} \qquad (59)$$

Thus ψ' is formed by adding to ψ a small amount of the state ψ_a^t , which arises from the excitation of an electron from ψ_a to ψ_t.

For ψ to be the best orbital of its type c_t must be zero, and this further requires that the Hamiltonian integral between ψ and ψ_a^t be zero.

By substitution of equation(59) into the Schrodinger equation we obtain:

$$(H - E)\psi + c_t (H - E)\psi_a^t = 0 \qquad (60)$$

Multiplying from the left by ψ_a^{t*} and integrating, gives:

$$\langle\psi_a^{t*}|H|\psi\rangle + c_t\langle\psi_a^{t*}|H|\psi_a^t\rangle - c_t E = 0 \qquad (61)$$

Now the Hamiltonian is Hermitian, and we are dealing with real functions, therefore:

$$\langle\psi_a^{t*}|H|\psi\rangle = \langle\psi|H|\psi_a^t\rangle = F_{at} \qquad (62)$$

Thus if $c_t = 0$, $F_{at} = 0$.

If equation(62) is expressed in terms of spin-orbitals, we find by the same method used to derive (54):

$$F_{at} = H_{at}^c + \sum_{s=a}^{k} 2\langle\psi_a(i)\psi_s(j)|\frac{1}{r_{ij}}|\psi_t(i)\psi_s(j)\rangle - \langle\psi_a(i)\psi_s(j)|\frac{1}{r_{ij}}|\psi_s(i)\psi_t(j)\rangle \qquad (63)$$

If ψ_i and ψ_j are eigenfunctions of F with different eigenvalues, then:[26]

$$\langle\psi_i|F|\psi_j\rangle = 0 \qquad (64)$$

Thus, for equation(63) to be zero for any spin-orbital, not just ψ_a, the ψ must be eigenfunctions of F.

The Hartree-Fock equations can now be written:

$$F = H^c + \sum_{s=a}^{k} (2J_s - K_s), \quad F\psi = E\psi \qquad (65)$$

where E is the orbital energy, J_s and K_s are Coulomb and

exchange operators defined as:

$$(J_s)_{at} = \langle \psi_a(i)\psi_s(j)|\frac{1}{r_{ij}}|\psi_t(i)\psi_s(j)\rangle \qquad (66)$$

$$(K_s)_{at} = \langle \psi_a(i)\psi_s(j)|\frac{1}{r_{ij}}|\psi_s(i)\psi_t(j)\rangle \qquad (67)$$

The potential governing the SCF orbitals therefore consists of the core potential, and the Coulomb and exchange potentials for each electron. The operator F depends on all occupied orbitals ψ_i through the dependence of operators J_s and K_s on ψ_i. Thus an iteration method has to be adopted to calculate the SCF orbitals, and the condition of self-consistency is reached when the orbitals are consistent with the potential from which they were determined. The ground state is then represented by the best determinantal wave function and as such cannot be improved by configurational interaction with any singly-excited state.

From (63) the orbital energies can be expressed as:

$$E_r = F_{rr} = H^c_{rr} + \sum_{s=a}^{k}(2J_{rs} - K_{rs}) \qquad (68)$$

If the SCF orbitals are to be represented by the LCAO approximation, (25) must be substituted into (63). Thus,

$$F_{\mu\nu} = H^c_{\mu\nu} + \sum_{s=a}^{k}\sum_{\rho}\sum_{\sigma} c_{\rho s}c_{\sigma s}[2\langle\phi_\mu(i)\phi_\rho(j)|\frac{1}{r_{ij}}|\phi_\nu(i)\phi_\sigma(j)\rangle - \langle\phi_\mu(i)\phi_\rho(j)|\frac{1}{r_{ij}}|\phi_\sigma(i)\phi_\nu(j)\rangle] \qquad (69)$$

The SCF orbitals for a closed-shell system in this form are then determined by solving the secular equations:

$$\sum_{\upsilon} c_{\upsilon} (F_{\mu\upsilon} - ES_{\mu\upsilon}) = 0 \qquad (70)$$

through the determinant:

$$|F_{\mu\upsilon} - ES_{\mu\upsilon}| = 0 \qquad (71)$$

These are known as Roothaan 's equations.[27]

6. The Semi-Empirical SCF ASMO Method[28,29]

During 1953 a series of papers was published which introduced a semi-empirical element into the SCF ASMO methods, in order to simplify them yet still retain a certain degree of rigour. The theory was developed independently by Pariser and Parr[28] and Pople[29] and is called the Pariser-Parr-Pople SCF MO method.

In Hückel theory, AO 's are taken as orthogonal. The natural extension of this approximation to the two-centre integrals is to neglect any integral which contains an overlap density. This is known as the zero-differential-overlap approximation.[30] This means that $\langle \mu\lambda|G|\upsilon\sigma\rangle$ is neglected unless $\mu = \upsilon$, $\lambda = \sigma$.

In Pople 's treatment, the σ-electron system is treated as a non-polarisable core, and its effect is included in the $H^{c}_{\mu\upsilon}$ term. (equation 69) Thus,

$$H^{c}_{\mu\upsilon} = -\frac{1}{2}\nabla^2 + \sum_{\rho} V_{\rho}(r) \qquad (72)$$

where $V_\rho(r)$ represents the potential due to the nuclear charge and all the σ-electrons associated with atom ρ.

$H^c_{\mu\mu}$ can be written as:

$$H^c_{\mu\mu} = \langle \phi_\mu | -\tfrac{1}{2}\nabla^2 + V_\mu | \phi_\mu \rangle + \sum_{\alpha \neq \mu} \langle \phi_\mu | V_\alpha | \phi_\mu \rangle \qquad (73)$$

The first term is equated to the ionisation potential I_μ appropriate to the particular valence state of the atom in the molecule. The second term was originally estimated using a point-charge model as:

$$\langle \phi_\mu | V_\alpha | \phi_\mu \rangle = - Z_\alpha R^{-1}_{\mu\alpha} \qquad (74)$$

where Z_α is the effective charge of the σ-core of atom α, $R_{\mu\alpha}$ is the distance between μ and α. Similarly the nuclear repulsion energy was expressed as:

$$\sum_{\mu<\upsilon} R^{-1}_{\mu\upsilon} Z_\mu Z_\upsilon \qquad (75)$$

For hydrocarbons, $Z_\mu = 1$, but it takes different values for heteroatoms.

In a later paper[31] they used a more logical procedure. $\langle \phi_\mu | V_\alpha | \phi_\mu \rangle$ was evaluated by assuming that the energy of a density ϕ_μ^2 in the field of a distant core of net charge Z_α, is equal and opposite in sign to the energy of ϕ_μ^2 in the field of a distant charge $Z_\alpha \phi_\alpha^2$. Thus,

$$\langle \phi_\mu | V_\alpha | \phi_\mu \rangle = - Z_\alpha \langle \phi_\mu \phi_\alpha | G | \phi_\mu \phi_\alpha \rangle \qquad (76)$$

$$\langle \phi_\mu | V_\alpha | \phi_\upsilon \rangle = - Z_\alpha \langle \phi_\mu \phi_\alpha | G | \phi_\upsilon \phi_\alpha \rangle \qquad (77)$$

which is neglected in the zero-overlap approximation.

Introducing the three expressions:

$$\text{bond order, } p_{\mu\upsilon} = \sum_i 2c_{\mu i} c_{\upsilon i} \qquad (34)$$

$$\text{charge density, } q_\mu = \sum_i 2c_{\mu i}^2 \qquad (33)$$

$$\text{resonance integral, } H^c_{\mu\upsilon} = \begin{cases} \beta_{\mu\upsilon} \text{ for neighbouring atoms} \\ 0 \text{ otherwise} \end{cases}$$

equation(69) becomes:

$$F_{\mu\mu} = I_\mu + \tfrac{1}{2} q_\mu \gamma_{\mu\mu} + \sum_{\alpha \neq \mu} (q_\alpha - Z_\alpha) \gamma_{\mu\alpha} \qquad (78)$$

$$F_{\mu\upsilon} = \beta_{\mu\upsilon} - \tfrac{1}{2} p_{\mu\upsilon} \gamma_{\mu\upsilon} \qquad (79)$$

where

$$= \langle \phi_\mu(i) \phi_\upsilon(j) | \tfrac{1}{r_{ij}} | \phi_\mu(i) \phi_\upsilon(j) \rangle \equiv \langle \mu\upsilon | \mu\upsilon \rangle \qquad (80)$$

The total pi-energy of the normal state of a molecule including nuclear interaction is:[27]

$$E = 2 \sum_\mu H^c_{\mu\mu} + \sum_\mu \sum_\upsilon (2J_{\mu\upsilon} - K_{\mu\upsilon}) + V_{nn} \qquad (81)$$

$$= \tfrac{1}{2} \sum_{\mu\upsilon} p_{\mu\upsilon} (H^c_{\mu\upsilon} + F_{\mu\upsilon}) + V_{nn} \qquad (82)$$

when the MO 's are written in LCAO form. To be consistent with equations(76) and (77), the core repulsion energy is approximated as:

$$V_{nn} = Z_\mu Z_\upsilon \sum_{\mu<\upsilon} \sum \langle \phi_\mu \phi_\upsilon | \phi_\mu \phi_\upsilon \rangle \qquad (83)$$

where the repulsion between the cores of atoms μ, υ is treated as the repulsion between charges Z_μ, Z_υ occupying the p-AO 's ϕ_μ, ϕ_υ.

With these approximations, the total pi-energy of a ground state closed-shell configuration in the Pople method can be written as:

$$E_\pi = \sum_\mu p_{\mu\mu}\left(I_\mu + \frac{1}{4} p_{\mu\mu}\gamma_{\mu\mu}\right) + 2\sum\sum_{\mu<\upsilon} p_{\mu\upsilon}\beta_{\mu\upsilon} + \sum\sum_{\mu<\upsilon}\left[(p_{\mu\mu} - Z_\mu)(p_{\upsilon\upsilon} - Z_\upsilon) - \frac{1}{2} p_{\mu\upsilon}^2\right]\gamma_{\mu\upsilon} \qquad (84)$$

The pi-bonding energy can be written:

$$E_{\pi b} = -\left[\sum_r E_r - nI_\mu + V_{nn}\right] \qquad (85)$$

Thus the pi-bonding energy of a ground state closed-shell configuration in the Pople method is:

$$E_{\pi b} = -\left[2\sum\sum_{\mu<\upsilon} p_{\mu\upsilon}\beta_{\mu\upsilon} + \frac{1}{4}\sum_\mu q_\mu^2\gamma_{\mu\mu} + \sum\sum_{\mu<\upsilon}(q_\mu - Z_\mu)(q_\upsilon - Z_\upsilon)\gamma_{\mu\upsilon} - \frac{1}{2}\sum\sum_{\mu<\upsilon} p_{\mu\upsilon}^2\gamma_{\mu\upsilon}\right] \qquad (86)$$

7. Calculation of Matrix Elements

a) The one-centre integrals, $\gamma_{\mu\mu}$

Pariser and Parr[28] calculated $\gamma_{\mu\mu}$ using an argument based on the energy change in the process:

$$2C \rightarrow C^+ + C^-$$

$$tr\,tr\,tr\,\pi \qquad tr\,tr\,tr \qquad tr\,tr\,tr\,\pi^2$$

Assuming that the cores of the C atoms remain unchanged, and that the transfer involves a pi-electron,

the process should be endothermic by an amount $\gamma_{\mu\mu}$. Experimentally this energy is given by the valence state ionisation potential I of neutral carbon minus its electron affinity E. Thus:

$$\gamma_{\mu\mu} = I - E \qquad (87)$$

The value estimated empirically in this way is 10.53 eV[28], compared with the value 16.93 eV calculated using Slater orbitals.[32] Pariser and Parr attributed this discrepancy to their failure to consider the change in σ-electron energy when forming C^+ and C^- from 2C, though it was later suggested by Dewar and Wolfnung[33] that the lower empirical value might be due to electron correlation, the electrons in a pi-system tending to stay on opposite sides of the nodal plane. Using Slater orbitals, Snyder and Parr[34] tested this idea by breaking repulsions between full pi-orbitals into repulsions between individual lobes of pi-orbitals. The theoretical $\gamma_{\mu\mu}$ for carbon, 16.93eV, was found to be the mean of the theoretical $\langle \mu_u \mu_u | \mu_l \mu_l \rangle$, 10.98eV, and the theoretical $\langle \mu_u \mu_u | \mu_u \mu_u \rangle$, 22.89eV, where the subscripts u, l denote upper and lower lobes, respectively. The fact that $\langle \mu_u \mu_u | \mu_l \mu_l \rangle$ is close to the empirical value supports the idea of electron correlation. Pariser obtained the better empirical value, $\gamma_{\mu\mu}$ = 10.96eV, from the benzene spectrum.[35]

$\gamma_{\mu\mu}$ for two electrons is the net energy spent in the

process:[36]

$$2A^{+} \rightarrow A^{2+} + A$$

Thus:

$$\gamma_{\mu\mu} = I_2 - I_1 \qquad (88)$$

where I_2 and I_1 are the second and first valence state ionisation potentials of the atom in question.

b) The two-centre integrals, $\gamma_{\mu\nu}$

A simple idea proposed by Mataga and Nishimoto[37] may be applied to obtain these integrals. The semi-empirical representation for $\gamma_{\mu\nu}$ is assumed as follows:

$$\langle \mu\mu | \frac{1}{r_{\mu\nu}} | \nu\nu \rangle = \frac{e^2}{a + r_{\mu\nu}} \qquad (89)$$

where $r_{\mu\nu}$ is the interatomic distance between μ and ν. Parameter a is determined using the valence state ionisation potential I and electron affinity E in the same valence state.[38] For the homonuclear case:

$$\gamma_{\mu\mu} = \frac{e^2}{a} = I_\mu - E_\mu \qquad (90)$$

For the heteronuclear case:

$$\frac{e^2}{a} = \frac{\gamma_{\mu\mu} + \gamma_{\nu\nu}}{2} \qquad (91)$$

c) The resonance integral, $\beta_{\mu\nu}$

The resonance integral is considered to be constant for a given bond and depends on the bond length and the valence state of the two atoms. From equation(72),

$$H^{c}_{\mu\upsilon} = \langle \phi_\mu | -\frac{1}{2}\nabla^2 + V_\mu + V_\upsilon | \phi_\upsilon \rangle \qquad (72a)$$

Now $\langle \phi_\mu | -\frac{1}{2}\nabla^2 + V_\mu | \phi_\mu \rangle$ has already been equated to the valence state ionisation potential I_μ, for removing a pi-electron from atom μ. $\langle \phi_\mu | \phi_\upsilon \rangle$ is an overlap integral, $S_{\mu\upsilon}$, and a reasonable approximation for $H^{c}_{\mu\upsilon}$ is:

$$H^{c}_{\mu\upsilon} \propto S_{\mu\upsilon}(I_\mu + I_\upsilon)$$

or
$$H^{c}_{\mu\upsilon} = kS_{\mu\upsilon}(I_\mu + I_\upsilon) \qquad (92)$$

which is the Mulliken-Wolfsberg-Helmholtz equation.[39,40] In this equation, k is a constant which is evaluated from the C-C bond in benzene. The overlap integrals are evaluated using established master formulae[41] for Slater orbitals.

According to Dewar and Chung[42], H_{CC} differs for computation of ground and excited state properties, and the appropriate value must be chosen for the property being studied.

d) <u>The core integral, $H^{c}_{\mu\mu}$</u>

$H^{c}_{\mu\mu}$ for carbon has already been equated to the valence state ionisation potential. When two electrons are given to the pi-system by one atom, the energy of one of these electrons depends upon the attraction of the nucleus (which may be equated to the first valence state ionisation potential) and the repulsion of the other electron. Thus:

$$H^{c}_{\mu\mu} = I_1 + \gamma_{\mu\mu} = I_2 \text{ (from(88))} \qquad (93)$$

C. Symmetry Considerations

The symmetry properties of molecules are very important in configurational interaction and in determining the spectral selection rules. Each MO must transform as one of the irreducible representations (I.R.) Γ of the group to which the molecule belongs.

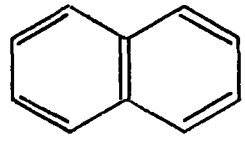
As an example, naphthalene belongs to the group D_{2h}. Half of the symmetry species of this group are symmetrical to reflection in the yz plane and the other half are antisymmetric. The σ MO 's belong to the former and the pi MO 's to the latter. In a discussion of pi MO 's, these orbitals are distinguished from one another by their behaviour under the three 2-fold rotations of the group. Hence the pi MO 's can be separated into different symmetry species by considering the sub-group D_2 which possesses the following symmetry elements:

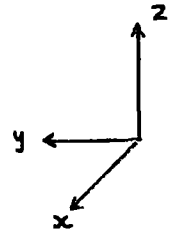
i) I - the identity operator

ii), iii), iv) C_2^z, C_2^y, C_2^x - a rotation by 180° about the z, y, or x axis of rotation, respectively.

The D_2 character table is:

D_2	I	C_2^z	C_2^y	C_2^x
A_1	1	1	1	1
B_1	1	1	-1	-1
B_2	1	-1	1	-1
B_3	1	-1	-1	1





Each MO transforms as an I.R. obtained by performing the operations (i)-(iv) on it. Thus in naphthalene the 10 MO 's comprise: $2A_1 + 2B_1 + 3B_2 + 3B_3$. In the full D_{2h} group these become: $2A_{1u} + 2B_{1g} + 3B_{2g} + 3B_{3u}$.

The symmetry of the total wave function for the ground or excited states is obtained as the direct product of the I.R. 's to which the individual MO 's belong. The pi-electronic ground state of naphthalene consists of 5 doubly-occupied MO 's $\Psi_1(A_{1u})$, $\Psi_2(B_{3u})$, $\Psi_3(B_{2g})$, $\Psi_4(B_{1g})$ and $\Psi_5(B_{3u})$, and hence the symmetry of the ground state is A_1 and it belongs to the I.R. $\Gamma.A_1$.

In the Schrodinger equation, the Hamiltonian operator is invariant under all symmetry operations and belongs to the totally symmetric I.R. $\Gamma.A_1$.

Consider the integrals:

$$\underset{(i)}{\langle \Psi_i^{-a} | \Psi_j^{-b} \rangle} \qquad \underset{(ii)}{\langle \Psi_i^{-a} | H | \Psi_j^{-b} \rangle}$$

where Ψ_i^{-a}, Ψ_j^{-b} are singly-excited electron configurations. These functions transform as the direct product of the I.R. 's of the AO 's i,a and j,b respectively. Integral(i) will be zero unless there is a component which transforms as $\Gamma.A_1$; for all other components, the positive and negative regions will cancel in the integration over all space. Thus Ψ_i^{-a} and Ψ_j^{-b} must transform as the same I.R., otherwise their direct product cannot give rise to a representation

containing $\Gamma.A_1$. Similarly, for integral (ii) the direct product of Ψ_i^{-a} and Ψ_j^{-b} must transform like $\Gamma.A_1$ or as a sum of components containing $\Gamma.A_1$. Thus Ψ_i^{-a} and Ψ_j^{-b} must belong to the same I.R. of the group if (ii) is to be non-zero.

9. The Intensities of Electronic Transitions

a) Theoretical treatment

A molecule which is initially in a state Ψ_k can absorb light of frequency υ, providing there is a state Ψ_n which has an energy greater than Ψ_k by an amount

$$\Delta E = E_n - E_k = hc\upsilon \qquad (94)$$

If this condition is fulfilled, the probability of a photon being absorbed depends on the magnitude of the transition dipole moment between the two states, $\underline{M}_{kn}$, which is defined by the integral:

$$\underline{M}_{kn} = e\langle \Psi_k | \Sigma_i Z_i \underline{r}_i | \Psi_n \rangle \qquad (95)$$

where $\underline{r}_i$ is the position vector of the ith particle (electron or nucleus) of charge $Z_i e$ in the molecule. If k=n then $\underline{M}_{kk}$ is the dipole moment in the state Ψ_k; it is usual to call $\underline{M}_{kn}$ the transition moment.

$$\underline{M}_{kn}^2 = (\underline{M}_{kn}^x)^2 + (\underline{M}_{kn}^y)^2 + (\underline{M}_{kn}^z)^2 \qquad (96)$$

The principles which were formulated in the previous section can now be applied to decide if all three components of the transition moment are zero(a forbidden trans-

ition), or if one of them(a plane-polarised transition), or two of them(x-, y-, or z-polarised transition) are zero.

To the approximation that the spin wave functions are independent of the coordinate wave functions, the spin operators S_z, S^2 commute with the vectors $\underline{x}$, $\underline{y}$ and $\underline{z}$, so there can only be non-zero matrix elements between functions corresponding to the same eigenvalues of S_z and S^2. [26] This gives the selection rule that only transitions between functions of the same multiplicity are allowed.

The coordinate axes x, y and z each transform as I.R. 's of the symmetry group of the molecule. Thus if the transition moment is to be non-zero, the direct product $\Psi_k \Psi_n$ must belong to the same I.R. as x, y or z. In the case of degeneracy the selection rule is: the transition moment is only non-zero when the direct product of initial and final state wave functions contains at least once the I.R. to which the x, y or z coordinate belongs.

It follows that for molecules with a centre of symmetry allowed transitions only occur between g- and u-states.

b) Experimental measurements

In order to measure the absorption spectrum of a molecule, the sample is placed in a cell at a known concentration and the ratio of the intensities of the transmitted and incident light is determined. This is given by:

$$\frac{I}{I_o} = 10^{-\epsilon c l} \qquad (97)$$

where ϵ is the extinction coefficient in $cm^{-1}mole^{-1}litre$.

A graph relating ϵ or $\log \frac{I}{I_o}$ for a specified concentration and cell length, to λ or υ is referred to as the absorption spectrum of the molecule. The maximum value of ϵ (ϵ_{max}) for a band is a rough measure of its intensity. However, a more precise and fundamental quantity than ϵ_{max} is the oscillator strength. This is proportional to the integrated intensity of the absorption band. Thus:

$$f = 4.319 \times 10^{-9} \int \epsilon \, d\upsilon \qquad (98)$$

10. Excited States and Configuration Interaction

If the ground state of energy E_o is a determinant of orthonormal orbitals:

$$\Psi_o = |\psi_1 \bar{\psi}_1 \cdots\cdots \psi_m \bar{\psi}_m| \qquad (20)$$

in which the lowest m orbitals are occupied, then promoting an electron from an occupied orbital ψ_k to an unoccupied orbital ψ_n will give rise to singlet and triplet states $^1\Psi_k^n$, $^3\Psi_k^n$, whose wave functions are given by equations (23) and (24).

Using the method described for the derivation of equation(54), the matrix elements of the total Hamiltonian H between the Ψ_K^n and Ψ_o can be reduced to one- and two-centre integrals. The results are:[43]

$$\langle {}^1\Psi_k^n | H | \Psi_o \rangle = \sqrt{2}\, F_{nk} \qquad (99)$$

$$\langle {}^1\Psi_k^n |H| {}^1\Psi_l^s\rangle - \delta_{kl}\delta_{ns}E_o = \delta_{kl}F_{ns} - \delta_{ns}F_{lk} + 2\langle ln|G|sk\rangle - \langle ln|G|ks\rangle \quad (100)$$

$$\langle {}^3\Psi_k^n |H| {}^3\Psi_l^s\rangle - \delta_{kl}\delta_{ns}E_o = \delta_{kl}F_{ns} - \delta_{ns}F_{lk} - \langle ln|G|ks\rangle \quad (101)$$

where $$F_{nk} = H^c_{nk} + \sum_{j=1}^{m}[2\langle jn|G|jk\rangle - \langle jn|G|kj\rangle \quad (102)$$

For SCF orbitals F_{nk} is diagonal, i.e. the ground state does not interact with singly-excited states.

$$\langle ln|G|sk\rangle = \sum_{\mu}\sum_{\upsilon} c_{k\mu}c_{l\mu}c_{n\upsilon}c_{s\upsilon} \quad (103)$$

If there are two or more excited states which belong to the same symmetry species and whose configurational excitation energies lie fairly close together, then in general no such single function is acceptable. An acceptable function can be formed as a linear combination of the excited states. Thus the singlet state resulting from the excitation of an electron from a closed-shell ground state may be written as:

$$^1\Psi_I = \sum_k \sum_n c_I^s(k\to n)\,{}^1\Psi_{k\to n} \quad (104)$$

the summations k and n ranging over occupied and unoccupied orbitals respectively. The energies of the final states and the state-mixing coefficients are obtained by diagonalising a CI matrix with elements given by (100).

The intensity of absorption of radiation on excitation to one of the above states as measured by its oscillator strength is given by:

$$f_{kn} = 4.703 \times 10^{29} \upsilon_{kn} \underline{M}_{kn}^{2} \qquad (\cdot 04)$$

where υ_{kn} is the average wave number of the absorption band in cm^{-1} and $\underline{M}_{kn}$ is in e.s.u. The oscillator strength is a dimensionless quantity which was defined originally as the ratio of the quantum mechanical and classical contributions of the transition k→n. For strongly allowed transitions f_{kn} is of the order of one.

CHAPTER 3

Molecular Orbital Theory and Chemical Reactivity.

Two main methods of approach have been used in discussing reactivities, which are associated with different parts of the reaction path. In isolated molecule approximations the model of the transition state is generally one in which the pi-system is perturbed to a relatively small degree by the attacking reagent, and is assumed to have a structure similar to the reactants. In localisation models, the reaction is assumed to proceed via a σ-complex, or Wheland intermediate[44], with a structure resembling the transition state. Thus the intermediate should be a better model than the reactants for the transition state.

From transition state theory[45], the rate constant k, for reactions in solution is given by:

$$k = \kappa \frac{RT}{Nh} e^{-\frac{\Delta F^{\ddagger}}{RT}} \qquad (1)$$

where κ, the transmission constant is usually taken as unity. R is the gas constant, N is Avogadro's number, T is the absolute temperature, h is Planck's constant and $\Delta F^{\ddagger}$ is the free energy of activation.

Replacing $\Delta F^{\ddagger}$ by its equivalent, $\Delta H^{\ddagger} - T\Delta S^{\ddagger}$, equation(1) becomes:

$$k = \frac{RT}{Nh} e^{-\frac{\Delta H^{\ddagger}}{RT}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \qquad (2)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the standard heat of activation and entropy of activation, respectively.

The rate constant can also be expressed as:

$$k = \frac{RT}{Nh} \frac{f^{\ddagger}}{f_A f_B \ldots} e^{-\Delta E_o^{\ddagger}/RT} \qquad (3)$$

where f_A, $f_B \ldots$ are the partition functions of the reactants, and $f^{\ddagger}$ is the partition function of the transition state. $\Delta E_o^{\ddagger}$ is the activation energy at 0°K.

For two similar reactions it is plausible that the ratios of the partition functions are almost the same. Thus:

$$\frac{k'}{k} = e^{-\Delta\Delta E_o^{\ddagger}/RT} \qquad (4)$$

It can be shown[46] that this relation holds when $\Delta S'^{\ddagger} = \Delta S^{\ddagger}$, but this condition is not necessary, and the equality of the ratios of the partition functions at a given temperature does not imply that the entropies of activation, which contain the derivative of the partition functions, should be the same.

$\Delta E_o^{\ddagger}$ can be written as $\Delta E_p^{\ddagger} + \Delta E_z^{\ddagger}$, where $\Delta E_p^{\ddagger}$ is the potential energy of activation per mole, and $\Delta E_z^{\ddagger}$ is the difference in zero-point energy between the reactants and the transition state. For large molecules, it will be reasonable to assume that $\Delta E_z'^{\ddagger} = \Delta E_z^{\ddagger}$ for two similar reactions. With these assumptions equation(4) can be written:

$$-RT \ln \frac{k'}{k} = \Delta\Delta E_p^{\ddagger} \qquad (5)$$

for a series of reactions carried out under similar conditions, provided that no specific effects, e.g. steric

hindrance, are involved.

For reactions involving changes in pi-electron systems, the pi-energy change is separated from the σ-energy change, steric and solvent effects etc. and it is assumed that $\Delta E_p^{\ddagger} \propto \Delta E_\pi$, the difference in pi-bond energy between reactants and products.

With these assumptions it is possible to discuss the relative reactivities of different positions in terms of pi-electron properties alone. The two main methods of discussing the variation of ΔE_π will now be reviewed.

') <u>The Isolated Molecule Method</u>

The isolated molecule approximation represents a more precise formulation of the widely used qualitative theory of organic reactions due to Ingold, Lapworth and Robinson.[47] It assumes that electrophilic and nucleophilic reagents attack preferentially at positions of high and low charge, respectively.

As a reagent approaches an aromatic compound a change in hybridisation from sp^2 to sp^3 occurs at the position of substitution, due to incipient σ bonding. This may be represented by a reduction in magnitude of the resonance integrals of all bonds proceeding from this position. The pi-energy change brought about by the changes in the resonance integrals $\beta_{\mu r}$, $\beta_{\mu s}$ etc., may be expanded as

a Taylor series, the first term being:

$$\delta E = \sum_r \frac{\partial E}{\partial \beta_{\mu r}} \delta\beta_{\mu r} \qquad (6)$$

$$= \sum_r 2p_{\mu r} \delta\beta_{\mu r} \quad \text{(from(40), ch.2)} \qquad (7)$$

where the summation is over all neighbours, r.

Assuming that the change in all resonance integrals is the same, $\delta\beta$, then this becomes:

$$\delta E = 2(\sqrt{3} - F_\mu)\delta\beta \qquad (8)$$

where F_μ is the free valence index as defined in equation (35), chapter 2. Hence the most reactive position initially will be that with the highest free valence.

The free valence has received only moderate acceptance as a reactivity index in radical reactions, even though it is comparable with other indices and is mathematically related to the corresponding localisation energy and to the self-polarisability.[25,48]

The attacking species must approach very closely to the conjugated system for the formation of an incipient σ bond. However, if this species is charged, the pi electron system will be polarised and the free valence index will not be valid. Wheland and Pauling[44] assumed that the effect of a charged reagent could be represented as a change $\delta\alpha_\mu$ in the coulomb integral at the position of attack μ. Again the pi energy change can be expanded as a power series in $\delta\alpha_\mu$:

$$\delta E = \frac{\partial E}{\partial \alpha_\mu}\delta\alpha_\mu + \frac{1}{2}\frac{\partial^2 E}{\partial \alpha_\mu^2}\overline{\delta\alpha_\mu}^2 + \ldots\ldots \qquad (9)$$

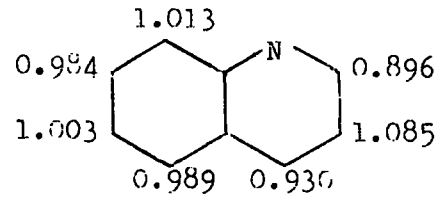
$$= q_\mu \delta\alpha_\mu + \frac{1}{2}\pi_{\mu\mu}\overline{\delta\alpha_\mu}^2 + \ldots\ldots \qquad (10)$$

where q_μ and $\pi_{\mu\mu}$ are defined as in equations (40), (43), chapter 2. From the definition of self-polarisability, the charge at position μ will be:

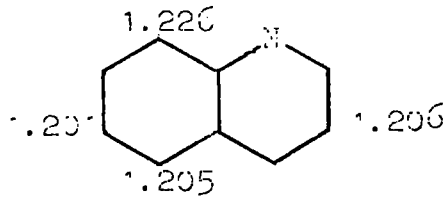
$$q_\mu^* = q_\mu + \pi_{\mu\mu}\delta\alpha_\mu \qquad (11)$$

The index q_μ alone would adequately describe the effect of a very small $\delta\alpha_\mu$, but a rough estimate of $\delta\alpha_\mu$ by Brown[49] shows that the polarising effect of an ion even two or three bond lengths away from μ may outweigh the effect of a heteroatom in the conjugated framework, and the two terms in equation (10) are then of comparable importance. This estimate shows that it would be an improvement of the isolated molecule approximation to consider changes in the coulomb integrals at atoms neighbouring the position of attack.

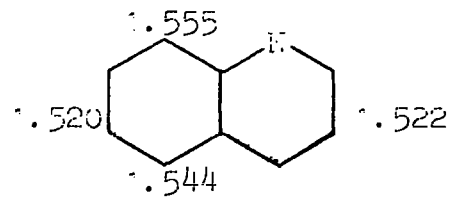
The effect of neglecting $\pi_{\mu\mu}$ can be seen by considering quinoline. The ground state charge distribution, taking $\delta\alpha_N$ for the heteroatom as $0.5\beta_o$, is:



This indicates 3>8>6 as the sequence of active positions although experimental data on nitration[50] and bromination[51] indicate that electrophilic substitution occurs exclusively, and almost equally, at positions 5 and 8. Taking $\delta\alpha_\mu$ as $0.5\beta_0$ and $1.5\beta_0$ respectively, Greenwood and McWeeny[52] calculated the charges at positions $\mu = 3, 5, 6$ and 8 due to polarisation by an attacking ion as below:



$\delta\alpha_\mu = 0.5\beta_0$



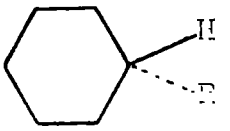
$\delta\alpha_\mu = 1.5\beta_0$

These results show that in the polarised molecules the charge builds up more rapidly at the site of attack when this is at position 5 or 8. Similar calculations of the change in pi energy show that as $\delta\alpha_\mu$ increases positions 5 and 8 become more active. This is strong evidence that when q_μ and $\pi_{\mu\mu}$ are considered together for systems in which the charge distribution is uneven in the ground state, the discrepancies that occur by considering the indices separately largely disappear. Qualitatively, $\pi_{\mu\mu}$ at position 4 may be compared with $\pi_{\mu\mu}$ in an α-naphthalene position, which will be greater than $\pi_{\mu\mu}$ in a β-position. Thus, for a large $\delta\alpha_\mu$ value, position 4 would be predicted as reactive if $\pi_{\mu\mu}$ were considered alone. However, the large

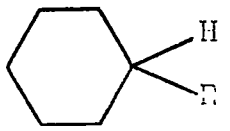
polarisability term does not compensate for the low charge $q_4 = 0.932$, arising from deactivation by ring nitrogen. In general, there is no more justification for using π_{rr} alone than for using q_r alone, an exception being alternant hydrocarbons, where all $q_r = 0$.[53]

2. The Localisation Energy Approximation

The localisation method was originally described by Wheland[54] with reference to resonance theory, the activated complex being considered as a resonance hybrid of structures including (i) and (ii) below:



(i)



(ii)

If the activated complex were similar to (i), the ease of reaction and preferred positions of substitution would be determined by the reactivity indices of the isolated molecule approximation. In structure (ii), the reagent is joined to the substrate by a covalent bond and the so-called 'residual molecule' (RM) is the conjugated system obtained by excluding the position of attack. Wheland considered the case where the activated complex was described by (ii) and assumed that the carbon atom under attack would be tetrahedral. The difference in energy of the pi-electrons in the unperturbed ground state and of the same

number of electrons in (ii) was defined as the localisation energy. In this approximation, each localised electron is assigned an energy α_0, corresponding to removal of its contribution to pi-bonding. For an alternant hydrocarbon, the localisation energy will be the same for radical or electrophilic attack. However, with the assumption that all σ-bond changes are regarded as constant in the transformation from the ground state to the intermediate, the localisation energy as estimated by Wheland should reflect the activation energy differences between different positions for any one type of reaction.

For example, the pi-electron energies of the neutral pi-electron system $(E_\pi)_A$ and the corresponding energy of the protonated system $(E_\pi)_{AH^+}$ may be calculated from Hückel theory. The difference of the two energies:

$$\Delta E_\pi = (E_\pi)_{AH^+} - (E_\pi)_A \qquad (12)$$

represents the localisation energy, although the effect of the positive charge is not dealt with by this theory. (Coulson and Dewar[55] have discussed the uncertainty in applying HMO theory to ions. It is probable that these difficulties are minimised in a comparison of structurally similar molecules.) Gold and Tye[56] calculated these energies for a series of aromatic hydrocarbons, assuming that the effect of the positive charge was of constant magnitude in the proton-addition complexes. The treatment allowed pred-

iction of the positions of protonation and of the relative basicities of structurally similar hydrocarbons in agreement with experiment. Mackor et al.[57] demonstrated that the reaction entropy is largely independent of the structure of the aromatic compound being protonated, by determining the thermodynamic data for some methylbenzenes and condensed aromatic hydrocarbons.

Thus:

$$\Delta F^{\ddagger} \sim \Delta H^{\ddagger} + \text{constant} = -RT\ln K_B^{*} \qquad (13)$$

where K_B^{*} is the reduced basicity constant (Gibbs-Helmholtz equation). The reduced basicity constant is the observed basicity constant K_B divided by the number of carbon atoms in the molecule which have the highest proton affinity, e.g. 6 in benzene, 4 in naphthalene etc.

Assuming that the σ-bonding energies are unchanged by the delocalisation, $\Delta H^{\ddagger}$ may be attributed to the change in pi-energy:

$$-RT\ln K_B^{*} = \Delta E_{\pi} + \text{constant} \qquad (14)$$

Thus a simple linear relationship exists between the localisation energy ΔE_{π} and $\ln K_B^{*}$. This was confirmed by Mackor et al.[57], who obtained a linear relationship:

$$\ln K_B^{*} = 26.4 \frac{\Delta E_{\pi}}{\beta} + \text{constant} \qquad (15)$$

with relatively small deviation. Similarly, Streitwieser[25] has shown that there is a linear correlation between the

cation localisation energy L_r^+, and experimental reactivities, with average deviation slightly lower than for the indices of the isolated molecule approximation.

Dewar 's approximate method for the conjugation energy between two odd-alternant hydrocarbon units can be applied to the calculation of localisation energies.[58,59]

Consider two odd-alternant radicals R, S combining to form R-S. Let H_R, H_S be the Hamiltonian operators determining the MO 's in R and S. Then the Hamiltonian operator for R-S, H_{RS} is:

$$H_{RS} = H_R + H_S + P \qquad (16)$$

where the perturbation P represents the formation of bonds between R and S in R-S. The basis of the method is that the function ψ, given by:

$$\psi = a\psi_R + b\psi_S \qquad (17)$$

can give a satisfactory approximation for certain orbitals of R-S. The energies associated with the orbitals(17) are obtained from the secular determinant:

$$\begin{vmatrix} H_{RR} - \varepsilon_{RS} & H_{RS} \\ H_{SR} & H_{SS} - \varepsilon_{RS} \end{vmatrix} = 0 \qquad (18)$$

where: $H_{RR} = \langle\psi_R|H_{RS}|\psi_R\rangle$, $H_{SS} = \langle\psi_S|H_{RS}|\psi_S\rangle$

$$H_{RS} = \langle\psi_R|H_{RS}|\psi_S\rangle = \langle\psi_S|H_{RS}|\psi_R\rangle = H_{SR}$$

Applying this method to the case of the non-bonding orbitals of energy $\varepsilon = \alpha$, of the odd-alternant radicals R, S, H_{RS} becomes:

$$H_{RR} = H_{SS} = \alpha \qquad (19)$$

Since ψ_R and ψ_S are the LCAO's:

$$\psi_R = \sum_l c_{lR}\phi_l \quad , \quad \psi_S = \sum_m c_{mS}\phi_m \quad ,$$

$$H_{RS} = \sum_l \sum_m c_{lR}c_{mS}\langle\phi_l|H_{RS}|\phi_m\rangle$$

Only one of the integrals $\langle\phi_l|H_{RS}|\phi_m\rangle$ is non-zero, and this is equal to β, the integral corresponding to the bond joining R to S. Thus:

$$H_{RS} = H_{SR} = c_{lR}c_{mS}\beta \qquad (20)$$

Solution of equation(18) gives:

$$\varepsilon_{RS} = \alpha \pm c_{lR}c_{mS}\beta \qquad (21)$$

where the positive combination represents bonding, β being negative. There are two electrons in the bond R-S formed from one electron in the NBMO of R and one electron in the NBMO of S. Thus the conjugation energy is given by:

$$\Delta E_\pi = 2\varepsilon_{RS} - (\varepsilon_R + \varepsilon_S) = 2\alpha + 2c_{lR}c_{mS}\beta - (H_{RR} + H_{SS})$$

$$= 2\,c_{lR}c_{mS}\beta \qquad (22)$$

where c_{lR} and c_{mS} are the coefficients of ψ_R, ψ_S in the NBMO.

If there is more than one link between R and S, the resonance energy is given by:

$$\Delta E_{\pi} = 2 \sum_{i} \sum_{m} c_{iR} c_{mS} \beta \qquad (23)$$

Now the localisation energy is equivalent to the conjugation energy between a single atom attached to two positions of the residual molecule, which is an odd-alternant hydrocarbon. If the position r to be localised is attached to positions s and t in the residual molecule,

$$\Delta E_{\pi} = 2\beta (a_{os} + a_{ot}) = N_r \qquad (24)$$

where N_r is Dewar's reactivity number[60]. a_{os}, a_{ot} are the NBMO coefficients which can be obtained by inspection.[61]

N_r values are smaller in magnitude than cation localisation energies L_r^+, but there is an excellent linear correlation between the two[25], and the correlation between N_r and experimental reactivities is slightly better than that given by L_r^+.

3. Frontier Orbitals and Charge Transfer Theories

It was suggested by Fukui et al.[62,63] that the electron density in the highest occupied ground state MO is important in determining the position of electrophilic attack, and the electron density in the lowest unoccupied ground state MO is important for nucleophilic attack. For radical reactions, both levels are taken into account and the Frontier Electron Density is the density of one electron in each or-

bital. These two orbitals he called Frontier Orbitals, and the frontier electron density f_r, has been used as a reactivity index to predict the active positions in a given molecule. Although this index predicts the most reactive sites with reasonable accuracy, it does not permit comparison between different hydrocarbons.

Whereas the isolated molecule and localisation methods were based on fairly well-defined physical models, there is little theoretical justification for frontier orbitals. Fukui et al. originally conceived them as participating in active triplet states[62], then as taking part in the formation of σ bonds at the position of attack[63]. Later they developed a theoretical treatment which was interpreted as a justification of the frontier electron theory.[64,48] They associated the frontier electron density with pi-electron changes similar to those used in isolated molecule approximations, but including the idea of hyperconjugation at the position of attack. The stability of the transition state was assumed to be increased by electron delocalisation between the pi orbitals of the hydrocarbon and a pseudo-pi-type orbital ψ_π^* associated with the attacking reagent X and the hydrogen atom H at the position r of attack. A roughly symmetrical arrangement of the centres H and X about the plane of the molecule was assumed, and the pseudo orbital given the form:

$$\psi_\pi^* = \frac{1}{\sqrt{2}} (\phi_X - \phi_H) \qquad (25)$$

where ϕ_X and ϕ_H are valence orbitals associated with atoms X and H. The symmetrical combination:

$$\psi_\sigma^* = \frac{1}{\sqrt{2}} (\phi_X + \phi_H) \qquad (26)$$

was assumed to overlap with the trigonal σ_r orbital of the carbon atom. Fukui used perturbation theory to derive an approximate expression for the change in pi energy of the hydrocarbon due to hyperconjugation:

$$\delta E = \sum_{j=1}^{n} \frac{(\upsilon_j - \upsilon) c_{rj}^2 \beta^{*2}}{\varepsilon_j - \alpha^*} + \upsilon(\alpha^* - \alpha_X) \qquad (27)$$

where α^* and α_X are the coulomb integrals associated with ψ_π^* and X, β^* is the resonance integral between ψ_π^* and ψ_r and is assumed small. The index j is taken over all MO's of the molecule under attack, and υ_j is the occupancy. υ is 0, 1 or 2 for electrophilic, radical or nucleophilic attack, respectively. The expression:

$$S_r = \sum_{j=1}^{n} \frac{(\upsilon_j - \upsilon) c_{rj}^2}{\varepsilon_j - \alpha_o} \qquad (28)$$

defined as the Superdelocalisability by Fukui[64], differs from the coefficient of β^{*2} in (27) by replacement of α^* by the standard coulomb integral α_c. This index is independent of the perturbation β^* and of the intrinsic properties of the reagent. Like other indices, it is defined in terms of the substrate alone. The correlation of S_r with reactivities is about as good as the other indices discussed.

The Fukui group then argued that since $|(\varepsilon_j - \alpha_o)|$ is least for the levels of the 2 frontier orbitals, which are

nearest to the zero of energy α_o, the summation S_r is dominated by these corresponding terms. Thus:

$$S_r^* = 2\frac{c_{rf}^2}{\lambda_f}, \quad \text{where } \lambda_f = |\varepsilon_f - \alpha_o| \tag{29}$$

and f indicates a frontier orbital. This proposal relates the model used to the frontier electron density, but the other terms in the summation are frequently almost as important, and the S_r^* approximation is questionable.

The performance of S_r as a reactivity index is often superior to that of others, with the possible exception of localisation energies, but there remains the deficiency that the physical interpretation of the role of frontier orbitals in reaction mechanisms is obscure, and attempts to give substance to Fukui 's treatment have frequently used questionable procedures or models.

Also closely related to the frontier electron theory are the several theories based on charge-transfer models of the transition state.[65,66] Brown 's model[66] for electrophilic reactions differs appreciably from that of Fukui et al. and leads to the definition of a new reactivity index Z_r.

A general wave function ψ_{CT} can be written as a linear combination of a wave function ψ_o, representing the unperturbed ground state, and functions ψ_j representing the configurations obtained by transfer of an electron from the jth MO to the vacant orbital of an attacking el-

Also, writing N as $-Z\beta_0$, (34) becomes:

$$\left[Z - 2\beta_e^{*2} \sum_j \frac{c_{rj}^2}{Z - Y_j} \right] \prod_k (Z - Y_k) = 0 \qquad (35)$$

Brown found that inclusion of configurations arising from charge-transfer from any but the highest MO had a negligible effect on the lowest charge-transfer state. Therefore all terms except the frontier orbital (j=f) term in (35) were dropped, and the Z_r value obtained from:

$$Z_r = Y_f + \frac{2\beta_e^{*2} c_{rf}^2}{Y_f} \qquad (36)$$

With assignment of reasonable values to Y_f and β_e^* for the best fit, Brown demonstrated a good correlation with Dewar's nitration data[58,66], the extent of correlation being better than for Dewar's N_r and Fukui's S_r indices.

The Z_r values for various positions in a conjugated hydrocarbon are determined primarily by Y_f and c_{rf}^2, the lower orbitals making little contribution except when one of them is nearly degenerate with the frontier orbital, therefore the frontier orbital density distribution c_{rf}^2 determines the position of attack.

Brown's method provides a physical basis for frontier electrons, which had been lacking in Fukui's theory. Frontier electron densities make a major contribution to S_r, but the proportional contribution from other occupied orb-

ectrophile.

$$\psi_{CT} = a_o\psi_o + a_1\psi_1 + \ldots\ldots a_j\psi_j + \qquad (30)$$

where charge transfer from σ orbitals is neglected.

The approximations of Hückel theory are introduced into the solution of the CI matrix to give:[67]

$$\left[W - \sum_{j(\neq 0)} \frac{H_{oj}^2}{W - \Delta_j} \right] \prod_{k(\neq 0)} (W - \Delta_k) = 0 \qquad (31)$$

where $W = H_{oo} - E$, $\Delta_j = H_{oo} - H_{jj}$ and H_{ij} is the matrix element between ψ_i and ψ_j of a Hamiltonian operator representing the charge-transfer complex. The CI integrals H_{oj} reduce to:

$$H_{jk} = 0; \quad H_{oj} = \sqrt{2} c_{j\mu} \beta_{j\mu} = \sqrt{2}\, c_{j\mu} g_e^{\neq} \beta \qquad (32)$$

$g_e^{\neq}$ is a constant characteristic of the electrophile.

The diagonal elements $\Delta_j = H_{oo} - H_{jj}$, relate to the formal transfer of an electron from the jth MO of the molecule under attack to the vacant orbital of the electrophile. This can be related to the ionisation potential I_j of the jth MO and the electron affinity E of the electrophile. Thus:

$$\Delta_j \sim E - I_j \qquad (33)$$

Writing E and I_j in terms of α_o and β_o, this becomes:

$$\Delta_j = (k_j - k_e)\beta_o = -Y_j\beta_o \qquad (34)$$

where k_j is calculated from the Hückel secular equations and k_e is characteristic of the electrophile.

itals to the latter are considerably greater than to Z_r values.

4. Comparison of Reactivity Indices

Streitwieser[25] has shown that the six reactivity indices discussed in this chapter correlate well with experimental reactivities. For alternant hydrocarbons, all six indices show fairly good correlation, with Dewar's reactivity numbers giving the best results. However, it has been shown[48] that the various indices are mathematically related, and therefore they are expected to be in agreement. In the case of alternant hydrocarbons it is therefore impossible to say that agreement between predicted and observed reaction rates, based on a particular index, point unambiguously towards a particular mechanism.

All of the indices discussed have been based on Hückel theory, or variants of it based on perturbation theory. This approach has been fairly successful in the case of hydrocarbons, but it becomes progressively less reliable for molecules containing increasing numbers of heteroatoms. Any treatment of reactivity that neglects the transition state is incorrect in principle, and the success of the isolated molecule indices is probably due to coincidences between the various quantities in question and the energy differences that determine the rates of reaction.

An obvious next step is to take the best method, i.e.

the localisation energy method, and re-examine it within the framework of the Pariser-Parr-Pople SCF MO theory.

5. Refined Treatments of Localisation Energies

In the calculation of cation localisation energies, the difference is taken of the pi electron energies of two separate pi systems, one of which is neutral and the other ionic. Eigenvalue solutions of secular equations derived for ions are known to yield inconsistent results, but a fairly successful technique for achieving self-consistency was introduced by Wheland and Mann.[68] The coulomb integral is replaced by a term

$$\alpha_r = \alpha_c + (1 - q_r) w \beta_0 \qquad (37)$$

where w is an empirical parameter. The charge distribution is obtained using the HMO method; this calculated distribution is then used to calculate new α's using (37), and the procedure repeated to self-consistency.

Ehrenson[69] calculated localisation energies of the methylbenzenes within the framework of the LCAO method, allowing for hyperconjugation between methyl groups and ring carbon atoms, following the calculations of Muller et al.[70] Essentially this was an SCF treatment of Hückel theory including overlap of neighbouring atoms and varying α's, β's, and S's to self-consistency. According to equation (14),

$$-RT \ln K_B^{\circ} = \Delta E_{\pi} + \text{constant}$$

If this equation is related to a standard equilibrium, it is possible to write:

$$- RT \ln \frac{K_B^{\neq}}{K_C^{\neq}} = \Delta G^{\neq} - \Delta G_o^{\neq} = \Delta\Delta E_\pi \qquad (38)$$

Using this purely hyperconjugative model, agreement between calculated values of $\Delta\Delta E_\pi$ and experimental ($pK_B^{\neq}$ - $pK_C^{\neq}$) values was not very good. In a later paper,[71] Ehrenson discussed the influence of an inductive effect and the combination of both effects. This latter combination gave values closely approaching the reliable experimental data of Mackor et al.[57]

The above theory takes account of electron interaction in a very crude way by recognising that the coulomb integral will be sensitive to the electron density on the atom in question. A much more satisfactory treatment would be one based on the Pariser-Parr-Pople SCF MO method.

Stuart and Kruizinga[72] repeated the localisation energy calculations of Gold and Tye[56] using HMO-SCF calculations as introduced by Roothaan and Pople[27,29]. They obtained an excellent linear correlation between ΔE_π and $pK_B^{\neq}$ for a series of condensed polycyclic hydrocarbons.

Fukui et al.[73] in 1959, calculated localisation energies of a series of alternant and non-alternant hydrocarbons, using a Pariser-Parr technique. They made two different assumptions: a) that the interaction between the localised

electrons and the residual molecule might be neglected, b) that the interaction might be treated as a perturbation.

Calculations by both methods gave good results for alternants, but there was a divergence for non-alternants when ΔE_π's calculated by either method were plotted against values obtained by the Hückel method.

Nesbet[74] demonstrated a linear relationship between localisation energies calculated by Hückel theory and those calculated by an SCF Pariser-Parr treatment (neglecting localised electrons-residual molecule interaction), but only three alternants were studied.

In 1962, Flurry and Lykos[75] calculated localisation energies within the framework of the Pariser-Parr-Pople method, treating the effect of methyl groups as purely inductive. They used Slater-type orbitals and allowed for the inductive effect by changing the 2p pi-orbital exponent of the substituted carbon atom, the change being estimated from the expression:

$$I_o - I_n = \frac{1}{2}\left(n\delta E \right)^2 - nK \qquad (39)$$

where I_o is the ionisation potential of an electron in the pi-AO, I_n is the corresponding value when n identical groups are attached, K is a constant containing various electron-interaction terms, and δE is the change in the exponent.

For the pi electron energy they used the expression:[23]

$$E_\pi = \sum_i q_i \alpha_i + 2 \sum_{i<j} P_{ij} \beta_{ij} \qquad (40)$$

where:

$$\alpha_i = \alpha_i^c + \frac{1}{2} q_i \langle ii|G|ii\rangle + \sum_{j \neq i} q_j \langle ii|G|jj\rangle$$

$$\beta_{ij} = \beta_{ij}^c - \frac{1}{2} P_{ij} \langle ii|G|jj\rangle$$

Using this model, they obtained excellent agreement between ΔE_π's and $(pK_R^+ - pK_0^+)$ values as measured by Hecker et al.[57], despite the neglect of core repulsion.

Chalvet et al.[76] calculated ΔE_π for all the non-equivalent positions of six alternant and eight non-alternant cyclic hydrocarbons by three different techniques: Huckel, Pariser-Parr, and Pariser-Parr iterated to self-consistency. The correlation between the three methods was good for alternants but poor for non-alternants. All three methods correctly predicted the most reactive position in each molecule (with the exception of phenanthrene), with respect to electrophilic, nucleophilic, and radical substitution, but the predicted reactivities of less reactive sites were at variance.

Dewar and Thompson[77] explain these disappointing results as being due to neglect of core repulsion. Chalvet et al. plotted ln k against the difference in pi-binding energy between the reactants and the intermediate arenium ions, rather than the difference in pi-bond energy. The pi-bond energy $E_{\pi b}$, of a molecule is given by:

$$E_{\pi b} = E_{\pi} + V_{nn} \qquad (4')$$

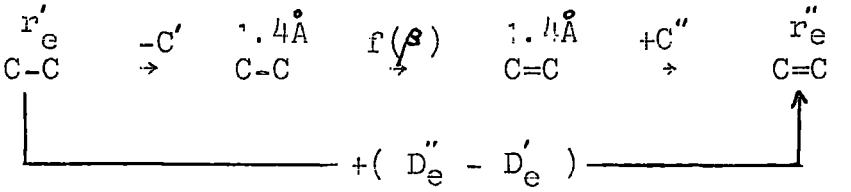
where E_{π} is the pi-binding energy and V_{nn} is the core repulsion. V_{nn} is different even for intermediates corresponding to substitution at different positions in the same hydrocarbon, thus the procedure of Chalvet et al. does not even lead to a correct prediction of relative isomer proportions.

In 1965, Dewar et al. published a series of papers[42,78] in which SCF MO theory was used to calculate ground state properties of conjugated hydrocarbons. The basic approach was the same as that described in chapter 2, i.e. a semi-empirical SCF MO treatment with neglect of overlap, following the general method for closed-shell molecules proposed by Pople.[29] The various integrals appearing in the Pople method were evaluated as follows:

a) The one-centre integral was taken as -10.98 eV, the evaluation being as described in chapter 2.[34]

b) The two-centre integrals $\gamma_{\mu\nu}$ were evaluated using the uniformly charged sphere model,[28,79] taking electron correlation into account.[34]

c) The one-electron resonance integrals $\beta_{\mu\nu}$ were estimated by the method of Dewar and Schmeising,[80] from the thermochemical cycle below:



D'_e , D''_e are the bond energies of a single bond and of a double bond respectively, between two sp^2 hybridised carbon atoms at their equilibrium bond lengths r'_e , r''_e. C', C'' are the compression energies required to change the bonds from their equilibrium lengths to a length of 1.4Å. $f(\beta)$ is the pi-bonding energy of a C=C bond of length 1.4Å and can be evaluated as:

$$f(\beta) = (D''_e - C'') - (D'_e - C') \qquad (42)$$

It can also be expressed theoretically as:

$$f(\beta) = -2\beta + \frac{1}{2} [\langle 11|11\rangle - \langle 11|22\rangle] \qquad (43)$$

in the Pople method. (from equation(36), chapter 2)

Using the data listed in their paper,[42] Chung and Dewar calculated β as -1.75eV. In addition, they determined from vertical resonance energies and transition energies, but the value obtained as above gave the best value for ΔH_f^o (benzene).

Using these parameters, they calculated the C-C bond energies for eleven benzenoid hydrocarbons and obtained the value 3.028eV ± 0.22%. However, calculated resonance energies for non-benzenoid hydrocarbons were only in fair agreement with experiment. In this treatment, all C-C bonds were assumed equal (1.397Å). Dewar and Gleicher[70] allowed for variations in bond length by recalculating bond orders $p_{\mu\nu}$, in each iterative cycle, and arranging for the bond lengths $r_{\mu\nu}$

and the integrals $\beta_{\mu\nu}$, $\gamma_{\mu\nu}$, to be recalculated from these values. Thus a set of MO's was obtained which was self-consistent for variations in the $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ with bond length. They assumed a linear relation between $p_{\mu\nu}$ and $r_{\mu\nu}$ as suggested by Dewar and Schmeising.[80]

$$r_{\mu\nu}\,(\text{in } \text{Å}) = 1.504 - 0.166\, p_{\mu\nu} \qquad (44)$$

The bond energies calculated by this method were almost identical to those calculated assuming constant bond length (3.820±0.2%), while those calculated using experimental bond lengths had a greater deviation (3.809 ± 0.34%). Bond lengths calculated by the self-consistent β procedure agreed with experimental values, within experimental error. The resonance and pi-bonding energies were calculated for the annulenes up to [30]annulene. All the [4n]annulenes were correctly predicted to be non-aromatic, while the [4n+2] annulenes were predicted to be aromatic up to and including [22]annulene, in agreement with the experimental work of Jackman et al.[81]

The success of this work, and of its preliminary application to heteroatomic molecules,[82] prompted Dewar and Thompson to examine its applicability in calculating chemical reactivities.[77] They used localization theory, and in order to make the approximations as valid as possible, selected reactions satisfying the following conditions:

a) The reactants and products were free from heteroatoms.

b) Reactions were chosen which were thought not to involve

any special resonance interactions in the transition state.

c) Series of reactions were chosen where adequate rate data were available.

They calculated ΔE_{π} using:

i) Hückel theory.

ii) Pariser-Parr-Pople(PPP) theory with all bond lengths equal (1.40Å).

iii) The PPP method made self-consistent for changes in bond length.

iv) The split-p-orbital(SPO) method[63] with all bond lengths equal.

v) The SPO method with self-consistent bond lengths.

The results obtained for methods (iv) and (v) were very similar to the results of (ii) and (iii) and will not be discussed further.

In order to examine the validity of the methods, they plotted graphs of ΔE_{π} against the logarithms of partial rate factors for nitrations in acetic anhydride at 0°C.[58] All the SCF MO methods gave better correlation than the Hückel method, with (ii) and (iii) giving slightly better correlation than (iv) and (v). In the treatments allowing for variations in bond lengths, the lengths of the C-C bonds in the intermediate were frequently quite different from those in the original molecule. They thought that the good correlation for fixed bond lengths might have been due

to the intermediate resembling reactants more closely than products. Therefore they calculated ΔE_π by a procedure where the bond lengths and $E_{\pi b}$ were estimated for the parent hydrocarbon, and $E_{\pi b}$ calculated for the intermediate arenium ion using the same values for the various integrals as in the final iteration for the parent hydrocarbon. In this case there was no linear correlation at all between log k and ΔE_π.

In the procedures using self-consistent bond lengths, the $\gamma_{\mu\nu}$'s are re-calculated for adjacent pairs but not for more distant pairs of atoms. For a neutral hydrocarbon, the errors are expected to be small, because the long range interactions appear in the diagonal elements of the F-matrix only in terms of the form $(q_\mu - 1)\gamma_{\mu\mu}$ (which vanish if atom μ is neutral), and in the off-diagonal elements in terms of the form $p_{\mu\nu}\gamma_{\mu\nu}$. (which are usually small because bond-orders between non-adjacent atoms are not large). However, in the intermediate a number of charge densities could be very different from unity and the lack of self-consistency in non-nearest neighbour $\gamma_{\mu\nu}$'s could interfere with estimates of $E_{\pi b}$ for the arenium ion. Until it is possible to determine the whole geometry of the molecule as a function of individual bond lengths, it is probably a better procedure to use the same bond lengths in initial and transition states. Dewar and Thompson found that it is better to allow for some variation in bond length than to assume all bonds

equal.

There were no experimental data available to plot ln f against ΔE_π for nucleophilic substitution, but plots of ΔE_π calculated for electrophilic substitution against values for nucleophilic substitution gave straight lines of unit slope with very little deviation.

ΔE_π values were plotted against ln f for substitution by methyl,[34] trichloromethyl,[35] and trifluoromethyl radicals.[36] In this case the treatments using self-consistent bond lengths gave a better correlation than the treatments using fixed bond lengths. For radical substitution, the intermediate is uncharged and the errors in the self-consistent treatment would be correspondingly smaller.

Similarly, they found linear correspondences between ΔE_π values and logarithms of relative rates of deuteration,[37] relative solvolysis rates of arylmethylchlorides,[38] and relative rates of exchange between chloride and iodide ions.[38] In these reactions there was little difference between the treatments using self-consistent bond lengths and the treatments using fixed bond lengths.

The above discussion shows that chemical reactivities can be treated successfully using localisation energies calculated within the framework of the PPP SCF MO method. It is possible to extend this treatment to substituted hydrocarbons using substituent constants evaluated from electronic spectra, as described in chapter 1. In the next section it will be shown how substituent effects can be incorporated into the PPP method, and how the theory is used to calculate ground and excited state properties of substituted aromatic hydrocarbons.

6. The Introduction of Substituent Effects into PPP SCF MO Theory

a) The σ-Inductive Effect

As described in section 7, chapter 2, values of $H_{\mu\mu}$ and $\gamma_{\mu\mu}$ are obtained from the appropriate valence state ionisation potentials and electron affinities, using the tables of Pritchard and Skinner or Jaffé and Hinze.[38] If there is any polarisation of σ electrons, these values must be modified. Ionisation potentials of isoelectronic series of atoms and ions show a quadratic dependence on the effective nuclear charge, as proposed by Glockler:[148]

$$I_\mu = AZ_\mu^2 + BZ_\mu + C \qquad (45)$$

where Z_μ is the effective nuclear charge of atom μ, and A, B and C are constants which can be determined by considering an isoelectronic series of ions. This formula is also applicable to the calculation of electron affinities. The

effective nuclear charge is a function of the electron density on atom μ, the dependence following directly from Slater's rules,[149] and so the fraction of the bonding electrons on μ must be determined. This is estimated by considering what fraction of the electron pair in any one single covalent bond between two atoms A and B is actually on A or B. The simplest estimate is to assume that the electron pair divides itself between A and B in the ratio of their orbital electronegativities.[150] Thus, of the two electrons in a single bond $2x_A/(x_A+x_B)$ electrons will be on atom A, x_A being the orbital electronegativity of A. The latter was shown by Mulliken[151] to equal $(I_A+ E_A)$, where I_A, E_A are the appropriate valence state ionisation potential and electron affinity.

When an atom or group of atoms is attached to atom μ in the ring, the calculations must take into account the changes in x_μ with electron density. Using an iterative procedure, a value of Z_μ is calculated (modified for the change in electron density using Slater's rules) and substituted into the appropriate quadratic equations to calculate new values of I_μ and E_μ. Using these values a new x_μ can be calculated, and the procedure repeated for the whole group of atoms until a self-consistent charge distribution has been obtained.

b) The pi-Inductive Effect

It has been suggested by Murrell et al.[3,5,15] and Craig and Doggett[4] that a substituent with two electrons in a pi orbital causes re-distribution of charge throughout a conjugated system by an extra mechanism which they call the pi-inductive,[3,5,15] or orbital penetration effect.[4] Using a localised orbital method which included a pi-inductive effect, Murrell et al. had considerable success in calculating pi-electronic transition energies. They suggest that a substituent X changes the core integral $H_{\mu\mu}$ by an amount $\alpha_\mu(X)$, the pi-inductive parameter. This pi-inductive effect may operate either by a field effect or an exchange mechanism, which is short range and is a consequence of the Pauli exclusion principle;[3,15] the latter appears to be the most important effect for most substituents.[3]

The values of $\alpha_C(X)$ determined by Murrell et al. are used to modify H_{CC} by an amount $\alpha_C(X)$:[5]

$$H_{CC}(X) = H_{CC} + \alpha_C(X) \qquad (47)$$

Murrell et al. have determined the pi-inductive parameters only for the carbon atom in the bond C-X, since X is not considered to be part of the conjugated system in the ground state and does not enter directly into their calculation. In the molecules studied in this thesis the amount of charge transfer from atom X is small (ca. 0.1 electrons), and it seems reasonable to assume that the ef-

fect of the pi-interaction proposed by Murrell for the case of an AO containing two electrons will still apply and that as a first approximation the same pi-inductive parameters can be used.[5] In the calculations the substituent X is considered to be part of the conjugated system, and the value of H_{XX} is modified by an amount $\alpha_X(C)$. If the pi-inductive parameters arise from the mutual repulsion of electrons, then the effect on H_{CC} and H_{XX} will be equal.

The value of $\alpha_C(X)$ is the total change in H_{CC} produced by substituting a hydrogen atom by X and so it includes the σ and pi inductive effects.

$$\alpha_C(X) = \alpha_C(X)^{\sigma} + \alpha_C(X)^{\pi} \qquad (48)$$

Thus, having calculated $\alpha_C(X)^{\sigma}$ by the method described in (a), $\alpha_C(X)^{\pi}$ can be calculated as $(\alpha_C(X) - \alpha_C(X)^{\sigma})$. By equating $\alpha_C(X)^{\pi}$ with $\alpha_X(C)^{\pi}$, the total inductive parameter can be determined for X. Although $\alpha_C(X)^{\pi}$ and $\alpha_X(C)^{\pi}$ are always of the same magnitude and sign, $\alpha_C(X)^{\sigma}$ and $\alpha_X(C)^{\sigma}$ are opposite in sign.

c) The Methyl Group

The methyl group may be considered as a pseudoatom situated at the position of the carbon atom, contributing 2 electrons to the pi-system through hyperconjugation. (ref. 15, p.211) The first valence state ionisation potential of this pseudoatom is taken as the first ionisation potential of methane, equal to 13.12eV.[152,153] Since the group elec-

tronegativity is inaccessible, parameters pertaining to the carbon atom are used. This seems reasonable since the carbon atom has effectively been given an artificial pi-bonding orbital. Thus,

$$\gamma_{\mu\mu}(\mathrm{Me}) = \gamma_{\mu\mu}(\mathrm{C{:}\ trtrtr\pi}) = 10.98 \text{ eV}$$
$$H_{\mu\mu}(\mathrm{Me}) = I_1(CH_4) + \gamma_{\mu\mu}(\mathrm{trtrtr\pi}) = 24.10 \text{ eV}$$

7. The Method of Calculation

The calculation of the self-consistent ground state of a molecule follows the sequence:

i) Solution of a matrix with guessed elements. (usually Hückel)

ii) Calculation of the density matrix.

iii) Assembly of the F matrix.

iv) Diagonalisation of the F matrix.

Steps ii)→iv) are repeated until the coefficients do not change on iteration.

The total pi-energy is computed from either of the equations 81 or 84. (chapter 2)

Having calculated the pi-bonding energies of the neutral molecules, the energies of the corresponding Wheland intermediates are calculated. For example, the Wheland intermediate for benzene is the benzenium cation. This is treated as a 5 carbon atom pi-system with 2 occupied orbitals. From the self-consistent density matrix, charge densities at each carbon atom are obtained, and the pi-bonding energy is computed as for the neutral species. The

localisation energy is then E_{π_b}(cation) - E_{π_b}(benzene).

For calculations on substituted cations, the inductive parameters of the substituents are multiplied by the charge density on the substituted carbon atom, obtained from the self-consistent density matrix of the appropriate unsubstituted cation.

Excited States

The energies of the excited states[43] are calculated by diagonalising the interconfigurational matrix whose elements are given by equations 100 and 101.(chapter 2)

Intensity Calculations

From equation 95, chapter 2, the transition moment between states Ψ_k , Ψ_n is given by:

$$\underline{M}_{kn} = e \langle |\Psi_k \sum_i Z_i \underline{r}_i \Psi_n| \rangle \qquad (49)$$

The calculation of $\underline{M}_{kn}$ is simplified by ignoring all those electrons of the configuration which remain in closed shells, only those electrons which are present in shells broken or formed during the transition being considered.[154]

Suppose the transition moment lies in the x direction only, for a transition from a doubly-filled orbital g to a vacant orbital e. Then:

$$\underline{M}^{x}_{ge} = e\langle \frac{1}{\sqrt{2}}|\psi_g(1)\overline{\psi}_g(2)|\,|x(1) + x(2)|\,\frac{1}{2}[|\psi_g(1)\overline{\psi}_e(2)| + |\psi_e(1)\overline{\psi}_g(2)|]\rangle \qquad (50)$$

which reduces, through the orthogonality of MSO's to:

$$\underline{M}^x_{ge} = \sqrt{2}\, e \langle \psi_g | x | \psi_e \rangle \qquad (51)$$

where the integration is over the space of one electron.

When the LCAO MO's are substituted into (51), terms such as $\langle \phi_\mu | x | \phi_\mu \rangle$ and $\langle \phi_\mu | x | \phi_\upsilon \rangle$ are encountered, which can be approximated as:

$\langle \phi_\mu | x | \phi_\mu \rangle = x_\mu$, the average value of x for μ.

$\langle \phi_\mu | x | \phi_\upsilon \rangle = \frac{x_\mu + x_\upsilon}{2} . S_{\mu\upsilon} = 0$, in the zero-overlap approximation.

For the state Ψ formed from a linear combination of configurations,

$$\Psi = \sum_i c_i \psi_i$$

$\underline{M}^x$ is given by,

$$\underline{M}^x = \sum_i c_i \underline{M}^x_i \qquad (52)$$

and

$$\underline{M}^2 = (\underline{M}^x)^2 + (\underline{M}^y)^2 + (\underline{M}^z)^2 \qquad (53)$$

where $\underline{M}^x_i$ is the value of the transition moment for each configuration ψ_i in the x direction.

Calculation of Ionisation Potentials

The wave function of an ionised state is obtained by ommitting one of the MO's from the ground state function, given by

$$^1\Psi_o = |\psi_1 \bar{\psi}_1 \ldots \bar{\psi}_n| \,, \quad (\text{eq. 20, chapter 2})$$

of energy

$$E(^1\Psi_o) = 2 \sum_i H_i + \sum_{ij} (2J_{ij} - K_{ij}) \quad (\text{eq. 54, ch. 2})$$

Consider the singly excited state obtained by removing either of the electrons occupying the MO ψ_i (assuming that ψ_i does not belong to a degenerate set). The wave function for this ionised state is:

$$^2\Psi_I = \psi_1\overline{\psi}_1 \cdots \psi_{i-1}\overline{\psi}_{i-1} \times \begin{bmatrix}\psi_i \\ \overline{\psi}_i\end{bmatrix} \psi_{i+1}\overline{\psi}_{i+1} \cdots \psi_n\overline{\psi}_n \qquad (54)$$

This state is a doublet, the two wave functions having the energy:

$$E(^2\Psi_I) = E(^1\Psi_o) - H_i - \sum_j (2J_{ij} - K_{ij}) \qquad (55)$$

(By the same method as for the derivation of eq. 54, ch. 2.) Hence the energy required for removing one of the electrons occupying ψ_i is given by:

$$E(^2\Psi_I) - E(^1\Psi_o) = - H_i - \sum_j (2J_{ij} - K_{ij}) \qquad (56)$$

$$= - E_i \quad \text{(from eq. 68, ch. 2)}$$

where E_i is the orbital energy.

It follows that $-E_i$ can be equated to the ionisation potential provided that the ionisation process is adequately represented by the removal of an electron from an orbital without change in the wave functions of the other electrons. (Koopman's theorem)

.....

The appropriate values of the parameters for various substituents, which were used in the calculations, are listed in table 1. The various integrals were evaluated using the methods described in chapter 2. The geometries

Table 1 Parameters and Integrals used in the Calculations. (Integrals in eV)

Substituent	r_{C-X}(Å)	γ_{XX}	H_{XX}	β_{C-X}	Inductive Parameters					
					$\alpha C(X)_\pi$	$\alpha C(X)_\sigma$	$\alpha X(C)_\pi$	$\alpha X(C)_\sigma$	$\alpha C(X)$	$\alpha X(C)$
Methyl	1.52	10.98	-23.63	-1.340	+0.47	0	+0.47	0	+0.47	+0.47
Fluorine[5]	1.30	21.01	-35.97	-1.785	+1.94	-0.86	+1.94	+1.16	+1.08	+3.10
Methoxy	1.37	19.27	-31.51	-1.680	+1.70	0	+1.70	+1.00	+1.70	+2.70
Hydroxy[5]	1.37	19.27	-31.51	-1.680	+1.70	0	+1.70	+1.00	+1.70	+2.70
Amino[5]	1.37	15.67	-24.86	-1.505	+2.37	-0.63	+2.37	+3.42	+1.74	+5.79
Chlorine[5]	1.71	13.03	-25.61	-1.523	+0.67	0	+0.67	0	+0.67	+0.67
Bromine	1.86	7.44	-19.20	-1.324	+0.37	0	+0.37	0	+0.37	+0.37
Iodine	2.06	6.55	-19.00	-1.212	+0.10	0	+0.10	0	+0.10	+0.10
Acetyl, Ar-C	1.50	10.98	-11.16	-1.460	-0.67	0	0	0	-0.67	0
C-O	1.23	15.20	-17.05	-1.860						
Nitro, Ar-N	1.49	16.32	-27.10	-1.126	-0.59	-0.49	0	+1.62	-1.08	+1.62
N-O	1.21	15.40	-17.67	-1.615						
Acetamido, Ar-N	1.43	16.54	-27.90	-1.309	0	-0.54	0	+0.82	-0.54	+0.82
N-C	1.33	10.98	-11.16	-1.554						
C-O	1.23	15.20	-17.02	-1.856						

In calculating excited state properties, the empirical β_{CC}=-2.371 was used,[35] and for ground state properties β_{CC}=-1.75 was used.[42] For C in a C-H bond, γ_{CC}=10.98eV, H_{CC}=-11.16eV.

of the compounds studied are generally unknown. The aromatic rings were assumed to be regular hexagons with C-C bond lengths 1.39 Å. C-X bond lengths were taken from, Tables of Interatomic Distances and Configurations in Molecules and Ions. (Spec. Pub. No. 11, Chem. Soc., London, 1958)

Program for Solution of Molecular SCF Problems[155]

The program was written in Algol 60 for the University of Newcastle English Electric KDF9 computer. The eigenvalues and eigenvectors of the Fock matrixes are found by the Wilkinson-Householder method[156]. The density matrix is then constructed from the eigenvector sets, and together with the core matrix and repulsion matrix is used to form a new F matrix. The iteration proceeds until the density matrix is self-consistent to 5 decimal places. For the excited states the interconfigurational matrix elements are calculated from equations '00 and 10', chapter 2, and the CI matrix so constructed is diagonalised. The program considers a prescribed set of single electron excitations and all CI between them. The oscillator strengths of the states are automatically calculated taking into account CI in the excited state. Finally, if required, the $n \rightarrow \pi^*$ transition energies are calculated using a similar technique to that employed for the pi-electronic states. For a molecule containing 10 pi electrons, e.g. naphthalene, the time taken is ca. 5 min.

CHAPTER 4

Electrophilic Aromatic Substitution.

1. The Mechanism of Electrophilic Aromatic Substitution.

Studies of the mechanism of electrophilic aromatic substitution have been divided into two main categories:

i) The study of the nature of the attacking group, or electrophile.

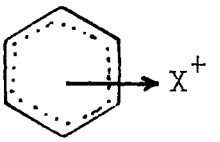
ii) The nature of the attack on the aromatic system and the role of σ- and pi complexes in the formation and disappearance of the transition state.

The electrophilic substitutions discussed in this thesis are all nitration reactions, and a discussion of the nature of the attacking species will be given in section 2.

At present there are two proposed mechanisms for electrophilic aromatic substitution,[28,29] and almost all such reactions occur by one or other mechanism. One mechanism[29] invokes a rate-determining formation of a pi-complex with subsequent different fast steps to form the several possible isomeric products. The second mechanism invokes formation of a σ-complex as the rate-determining step, which then gives only one possible isomeric product. In the first case the rate-determining step is prior to the product-determining step, while in the latter, the different isomers are formed by competing rate-determining steps. The first mechanism was proposed by Dish et al.[9] to explain electrophilic substitutions showing relatively small substrate selectivity. (Reactions with strong electrophiles, e.g. nitration by nitr-

onium salts,[91,92,93] ferric chloride or aluminium chloride catalysed brominations,[89] and certain Friedel-Crafts alkylations.[89,94,95]) An interesting feature of these reactions was the improbable values found for partial rate factors. (The partial rate factor f,[96] measures the reactivity of the position concerned relative to that of one position in benzene) For nitration of alkylbenzenes with nitronium tetrafluoroborate in tetramethylene sulphone, Olah found[91] values for f_m to be 0.14 for toluene, 0.14 for ethylbenzene and 0.10 for n-propylbenzene. These results were improbable, as there is no explanation for 10-fold deactivation of the meta-position relative to benzene. Partial rate factors can only be used if competition takes place between individual positions in an aromatic compound, and not between pi-electron systems as entities. In the competition between molecules involving their pi-systems as entities, the calculation of f-values is meaningless.

The pi-complex(i) contains a bond between the electrophile and the pi-electrons of the aromatic system and may be equivalent to a charge-transfer complex.

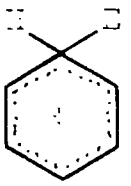


(i)

They are known to exist, both with ions such as A_g^+[97] and with neutral species such as iodine[98] and HCl.[99] In the

reactions mentioned above,[9] Olah et al. found that the observed relative reactivities of alkylbenzenes and benzene paralleled the relative stabilities of their complexes with Ag^+, I_2, Br_2 etc., which are known pi-complexing agents. The pi-electron density of the aromatic system would be little changed by the inductive and hyperconjugative effects of alkyl groups, and so the low substrate selectivity could be explained in terms of a rate-determining pi-complex formation.

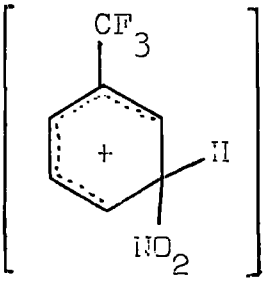
In the majority of electrophilic aromatic substitutions, there is high substrate selectivity and these reactions are adequately explained in terms of a rate-determining formation of a σ-complex (ii), or Wheland Intermediate.[54]



(ii)

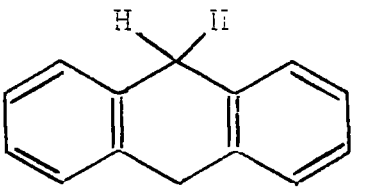
The substituted carbon atom has an approximately tetrahedral configuration (corresponding to sp^3 hybridisation), with the entering group E and the leaving hydrogen atom on opposite sides of the molecular plane. There is incontestable evidence for the formation of σ-complexes. In 1957 it was found by Olah et al.[55] that benzotrifluoride reacts with nitryl fluoride and boron trifluoride at -120° to give a coloured crystalline complex of mole ratio 1:1:1, which decom-

posed above -50° to give boron trifluoride, HF and m-nitrobenzotrifluoride in almost quantitative yield. They suggested the structure (iii) for the complex, and since m-nitrobenzotrifluoride is the product of nitration of benzotrifluoride under normal conditions, this was convincing evidence that (iii) is an intermediate in the nitration.



(iii)

Analogous complexes have been isolated using other electrophilic reagents.[101,102] The electronic spectrum of anthracene dissolved in sulphuric acid is similar to that of the benzhydryl cation, Ph_2CH^+, indicating the formation of (iv).



(iv)

A number of aromatic hydrocarbons dissolved in CF_3COOH and BF_3 indicate the presence of a methylene group such as (iv) contains.[103]

More general evidence that these cations are intermediates in electrophilic substitution was provided by Brown et al.[104], who showed that a plot of log k for the chlorina-

tion of methylbenzenes against log K for the equilibrium between the methylbenzenes and the cations they form with HF is linear. In addition, the rates of halogenation were found to parallel σ-complex, rather than pi-complex, stabilities. These results are consistent with the two-step mechanism:

$$Ar\text{-}H + E^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\overset{H}{\underset{E}{<}}{}^{+} \xrightarrow{k_2} Ar\text{-}E + H^+$$

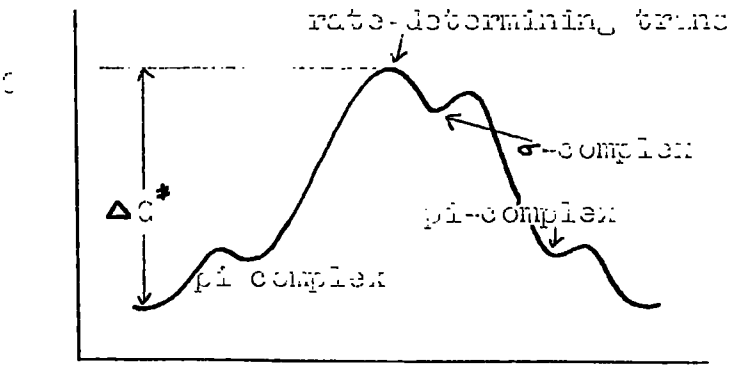
as first envisaged by Lapworth,[105] Pfeiffer and Wizinger,[106] and later by Wheland.[54] Synchronous formation of a C-E bond and cleavage of a C-H bond has been dismissed as a result of the above work on intermediates and Melander's demonstration of the absence of a kinetic isotope effect in nitrations of aromatic compounds.[107] Similar results were found for different benzenoid compounds under nitrating conditions varying from pure nitric acid to a solution of nitric acid in oleum.[108,109] In the above scheme, no isotope effect would be detected if $k_2 \gg k_{-1}$.

Positive isotope effects have been observed for sulphonation,[107,110] diazonium coupling,[111] and the iodination of phenol and aniline.[112,113] Although this could be accounted for by the concerted mechanism, kinetic evidence points to the two-step mechanism in which k_2 is comparable with or $< k_{-1}$.[111]

A recent communication by Myhre et al.[114] has shown evid-

dence for a rate-limiting proton transfer in several 1-substituted 2,4,6-tri-t-butylbenzenes, with a corresponding positive isotope effect. This was attributed to an increase of non-bonded repulsion energy as H was replaced by a large electrophile at a sterically hindered site, thus differentially increasing the energy of step (2) with respect to step (-1) in the above reaction scheme. This is the first evidence of a rate-limiting proton transfer in aromatic nitration but is still consistent with the two-step mechanism.

Although a rate-determining formation of a σ-complex is favoured by the above evidence, it is quite possible that pi-complexes are formed prior to the rate-determining step. It is easy to show that an aromatic compound can form complexes with electrophilic reagents, but much harder to obtain kinetic evidence that such complexes are stages on the normal reaction path; however, the presence of pi- or charge-transfer complexes does not affect the free energy of the reaction as shown in the free energy profile below.



Thus the existence of low-energy pi-complexes does not affect the rate and need not be considered in theoretical treatments. The σ-complex serves as a good model for the transition state and will be used in the theoretical treatments in this thesis.

2. The Concept of the Nitronium Ion as the Active Nitrating Agent in Electrophilic Aromatic Nitrations.

It was first suggested by Euler[115] in 1903, and has since been supported by other authors,[116] that the active nitrating agent in electrophilic aromatic nitrations might be the nitronium ion NO_2^+, under certain conditions. The first experimental evidence that the nitrating agent was not merely the nitric acid molecule was due to Hantzsch.[117] He concluded as a result of cryoscopic and conductivity measurements that the nitric acid molecule was protonated to $(H_2NO_3)^+$, $(H_3NO_3)^{2+}$ and $(NO_3)^-$. In a mixture of nitric and sulphuric acid, the stronger sulphuric acid would protonate the nitric acid to form $(H_2NO_3)^+$ [or $(H_3NO_3)^{2+}$] and HSO_4^- ions. He proposed the formation of these ions to explain a three-fold increase (shown later to be 4-fold) in the freezing-point depression of sulphuric acid by nitric acid, relative to an ideal solution.

$$HNO_3 + 2H_2SO_4 \rightarrow H_3NO_3^{2+} + 2HSO_4^-$$

He also claimed isolation of crystalline perchlorates,

$[N_2NO_3]^+[ClO_4]^-$, $[N_3NO_3]^{2+}[ClO_4]^{2-}$.

In 1933 it was found by Chedin[117] that, in mixtures of nitric and sulphuric acid, two lines at 1400 and 1050 cm^{-1} were visible in the Raman spectrum. He also showed the presence of these lines in the spectrum of solid N_2O_5.[119] Susz and Briner[120] found the 1400 and 1050 cm^{-1} lines in the spectrum of N_2O_5 dissolved in nitric acid.

The nitronium ion was established as the active nitrating agent by Ingold, Hughes et al. in 1946.[121] Using improved cryoscopic methods, they found that the freezing-point depression of sulphuric acid by nitric acid was actually 4-fold and not 3-fold as found by Hantzsch. This was explained by further decomposition of the nitracidium ion:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

A further study of the interaction of nitric and perchloric acids showed the products to be $[NO_2]^+[ClO_4]^-$ and $[H_3O]^+[ClO_4]^-$.[122]

Cyoscopic,[123] conductimetric,[124] and Raman spectroscopic[123] measurements indicated that pure nitric acid contained NO_2^+ as a result of the ionisation:

$$2HNO_3 \rightarrow NO_2^+ + NO_3^- + H_2O$$

though the nitronium ion was only found in about 1% concentration.[123,125]

The study of the Raman and infra-red spectra of nitric acid/sulphuric acid mixtures[123] supported the complete con-

version of HNO_3 into $NO_2^+HSO_4^-$, whereas the extent of ionisation of pure nitric acid was slight. Solutions of nitric acid in acetic acid or nitromethane showed no trace of the nitronium ion. In sulphuric acid, the spectrum of nitric acid disappeared and was replaced by the lines at 1400 and 1050 cm^{-1} as found by Chédin. The 1400 cm^{-1} line was observed in solutions of nitric acid in perchloric and selenic acids[126] and in crystalline nitronium perchlorate.[123] The latter was known to be completely ionised into $[NO_2]^+$ and $[ClO_4]^-$,[124] so that the 1400 cm^{-1} line was attributed to $[NO_2]^+$. The 1050 cm^{-1} line was attributed to the $[HSO_4]^-$ ion in nitric /sulphuric acid mixtures, and to the $[NO_3]^-$ ion in N_2O_5/ nitric acid mixtures, since these anions absorb in that region. Because the $[NO_2]^+$ ion gave just one Raman line, it was assigned the linear structure: $O=\overset{+}{N}=O$.[126]

3. Kinetic Evidence to Establish the Nitronium Ion as the Reactive Entity in Aromatic Nitration.

(1) Nitrations in Aqueous Sulphuric Acid

The spectral evidence for the presence of the nitronium ion in solutions of nitric acid in aqueous sulphuric acid has already been presented above. That this is the reactive entity as opposed to the nitracidium ion was shown by the work of Westheimer and Kharasch,[127] Dunton and Malevi,[128] and Bennett et al.[129]

It was found[127,129] that the maximum rate of nitration, for a number of aromatic compounds, occurred at a definite acidity (as defined by Hammett's acidity function H_0[130]), rather than at a definite sulphuric acid concentration. The maximum rate was always around 90% sulphuric acid concentration, but addition of potassium bisulphate shifted the maximum to a slightly higher acid concentration (by lowering the acidity). The increase in nitration rate closely paralleled the ionisation of trinitrotritanol over a large concentration range, while the ionisation of anthraquinone was unrelated. There are two possible schemes for the ionisation of nitric acid in sulphuric acid:

$$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^- \qquad (1)$$

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (2)$$

As the ionisation of anthraquinone was known to follow scheme(1) and trinitrotritanol was known to follow (2),[130] these facts were interpreted as an indication that NO_2^+ is the effective nitrating agent in sulphuric acid solution.

For nitrations in partly aqueous sulphuric acid, second order kinetics were observed for fairly unreactive aromatic compounds.[123]

$$\text{Rate} = k_2 [ArH][HNO_3]$$

A sufficiently reactive aromatic compound should react with NO_2^+ as soon as it forms. In partly aqueous sulphuric/nitric acid mixtures, formation of NO_2^+ will be reversible

and the rate-determining step could then be the formation of NO_2^+, with the reaction rate independent of the nature or concentration of the substrate. Dunton et al.[120] observed zeroth-order kinetics with respect to reactive substrates in accordance with $v_3 >> v_2$ in the proposed reaction scheme:

$$HNO_3 + H^+ \underset{v_2}{\overset{v_-}{\rightleftharpoons}} NO_2^+ + H_2O$$

$$NO_2^+ + ArH \overset{v_3}{\rightarrow} ArNO_2 + H^+$$

For oxygen exchange via NO_2^+, the rate of exchange is the rate of formation, or destruction, of NO_2^+. The rate of nitration via NO_2^+ cannot exceed the rate of formation of NO_2^+, and it was found, for zeroth-order kinetics relative to the aromatic compound, that the rate of ^{18}O exchange between HNO_3 and H_2O paralleled, but slightly exceeded, the zeroth-order nitration rate. There was no evidence that nitration or exchange occurred by direct attack of $[H_2NO_3]^+$, though this could be a necessary precursor of NO_2^+.

(ii) Nitrations in Concentrated Sulphuric Acid.

Nitric acid is known to be completely ionised to NO_2^+ under these conditions,[123] and for unreactive aromatic compounds second-order kinetics are observed.[123, 127] Under these conditions the slow rate-determining step is attack of NO_2^+ on the aromatic compound. As already discussed, the nitration rate was found to increase up to 90% sulphuric acid concentration, due to the increase in ionisation of HNO_3

to NO_2^+, but above 90% concentration the rate decreased.

The rate should follow the equation:

$$\text{Rate} = k\,[NO_2^+][ArH]\,\frac{f_{NO_2^+}.f_{ArH}}{f^*}$$

Ingold et al.[123] suggested reasons why $\frac{f_{NO_2^+}}{f^*}$ should be a minimum in anhydrous sulphuric acid, and they gave evidence that, for nitro-compounds, f_{ArH} is greater in slightly aqueous sulphuric acid than in the anhydrous acid. Thus they were able to account qualitatively for the observed rate variation.

(iii) Nitrations in Organic Solvents.

Denford and Ingold[131] showed in 1938 that the kinetics of nitrations using excess of nitric acid in nitromethane or acetic acid were zeroth order with respect to the aromatic compound, if it was fairly reactive. For unreactive compounds, first-order kinetics were observed. For reactive aromatics the rate is therefore independent of their nature or concentration. The reaction rate was found to be constant until mono-nitration was complete. The rate-determining step was therefore limited to the nitric acid, with possible solvent assistance. They studied the effect of added potassium nitrate and traces of sulphuric acid. Due to the salt effect, an increase in reaction rate is usual with added salts, but a retardation was observed with a rate inversely proportional to $(a+b[NO_3^-])$, $[NO_3^-]$ being the

concentration of added nitrate ions, and a and b constants. The inference was that the added nitrate ion was repressing a necessary pre-equilibrium in which the nitrate ion is formed. This step could not be the direct formation of the nitrating entity, since zeroth-order kinetics were maintained even when the rate was retarded. Therefore they decided that the nitrate ion was repressing the formation of some precursor of the reactive species. They described the reaction as a two-step autoprotolysis:

$$2HNO_3 \xrightarrow{\text{fast}} [H_2NO_3]^+ + NO_3^-$$

$$[H_2NO_3]^+ \xrightarrow{\text{slow}} NO_2^+ + H_2O$$

As expected, the reaction was strongly catalysed by traces of sulphuric acid, due to preferential protonation by the stronger acid, and removal of NO_3^-.

$$HNO_3 + H_2SO_4 \rightarrow [H_2NO_3]^+ + HSO_4^-$$

$$NO_3^- + H_2SO_4 \rightarrow HNO_3 + HSO_4^-$$

Under the experimental conditions the autoprotolysis was too small to be detected spectroscopically.

The addition of small quantities of water had little effect on the zeroth-order rate because the pre-equilibrium step would not be affected. With the addition of more water, a competition would ensue between water and the aromatic compound for the nitronium ion, and first-order kin-

etics would be observed. Ingold and Hughes observed this change in acetic acid but not in nitromethane.[123, 132]

(iv) Nitrations in Pure Nitric Acid[123]

The kinetic observations were exactly as for nitrations in organic solvents. The addition of nitrate ions and of sulphuric acid both affected the rate appreciably. Since neither of these solutes would appreciably modify the concentration of molecular nitric acid, this was discounted as the reactive species.

4. The Reaction of the Nitronium Ion with the Aromatic Compound.

In nitration, a nitro-group is added to the aromatic ring as a nitronium ion and a hydrogen atom is eliminated as a proton. The kinetic evidence for the role of the nitronium ion gives no indication as to whether the reaction involves addition of NO_2^+ followed by elimination of H^+, or is a concerted process with synchronous formation of a C-N and breakage of a C-H bond.

The concerted mechanism was rejected as a result of the work of Melander,[107, 133] who found no kinetic isotope effect in the nitration of tritiated aromatic compounds. This was immediate proof that the C-H bond from which a proton is ultimately displaced is not weakened during the rate-determining step. Similar results were found later for deuterated compounds.[108, 109]

CHAPTER 5

The Nitration of Methyl-Substituted Benzenes and Naphthalenes.

Introduction

Before 1927 there was no information on relative reactivities of aromatic hydrocarbons towards nitration. In 1914, Hollemann[34] had measured the percentages of isomers formed in the nitration of toluene and reported approximately 59% ortho-, 4% meta- and 37% para-substitution. The first data on relative reactivities were published in 1927 by Ingold and Shaw,[35] who introduced the method of competitive reactions. The competitive method of comparing reaction rates does not require an accurate knowledge of the reaction kinetics, provided that both hydrocarbons are substituted by the same agent, and that the rates of substitution are of the same order with respect to the hydrocarbon concentrations. They defined the Coefficient of Activation F, as the number of molecules substituted during a small element of time at the given nuclear carbon atom, divided by the number of molecules that would have been substituted at the same carbon atom had the orienting group been absent. (This was later[36,37] given the name, partial rate factor, and the symbol f.) By nitration of an equimolar mixture of toluene and benzene with HNO_3/acetic acid, and measuring the density of the mixture of nitrobenzene and nitrotoluenes obtained, they found for the relative reactivity, $k_{toluene}/k_{benzene} = 15.7$. They calculated activity coefficients for toluene as $F_o = 27.6$, $F_p = 34.6$ and $F_m = 2.1$ by using Hollemann's data for iso-

mer distributions.

In 1931,[29] a more careful study was made of the competitive nitration of benzene and toluene under various conditions. Using nitric acid/nitromethane they measured $k_{Toluene}/k_{Benzene}$ = 21, f_o=37, f_m=2.0 and f_p=47 at 30°C.

With the advent of gas-liquid chromatography it became possible to make much more accurate measurements of isomer distributions. In 1960, Knowles et al.[36] studied the nitration of alkylbenzenes using equimolar quantities of fuming nitric acid (d=1.52) and acetic anhydride (effectively acetyl nitrate) at 0°. By using Ingold's value of 27 for $k_{Toluene}/k_{Benzene}$,[25] they re-calculated the partial rate factors as f_o=49.7, f_m=2.3 and f_p=50.0. These results were extended by Olah et al.[37] who, in a systematic study of aromatic nitrations, studied competitive nitrations between alkylbenzenes and benzene for a variety of solvents and reactants. At 25°, using nitric/acetic acid media, they obtained $k_{Toluene}/k_{Benzene}$ = 20.8 and the isomer distributions 59.9% ortho-, 2.8% meta- and 40.3% para-nitrotoluene. Olah's investigations of the nitration of the xylenes indicated that overall rates with respect to benzene were in excess of 1000 for both meta- and para-xylenes, results at variance with those for toluene and Alcorn and Wells's results for the monomethylnaphthalenes.[38] The nitration of the xylenes in acetic/nitric acid media has therefore been re-investigated, over a wide temperature range, to measure

isomer distributions, and partial rate factors relative to benzene. It was also of interest to investigate the introduction of a second methyl group into the naphthalene nucleus. Isomer distributions and partial rate factors have therefore been measured for 2,6-dimethylnaphthalene.

'. Calculation of Relative Rate Constants.

The competitive method of comparing reaction rates does not require an accurate knowledge of the reaction kinetics, provided that each competing substrate is always present in excess over the amount of reagent present, that all substrates react by the same mechanism, and that the reactions are kinetically first-order in substrate. The relative rate constants can then be determined as follows:

For the reaction of the nitrating agent X, with hydrocarbons HC. and HC_2 at time t,

$$\begin{aligned} \frac{d}{dt}[HC.]_t &= -k_1[X]_t^n[HC_1]_t \\ \frac{d}{dt}[HC_2]_t &= -k_2[X]_t^n[HC_2]_t \end{aligned} \qquad (1)$$

where [ ] represents molar concentrations. Here n is the order of reaction with respect to X, k_1 and k_2 are the rate constants for HC_1 and HC_2 respectively.

$$\frac{d[HC_1]_t}{d[HC_2]_t} = \frac{k_1[HC_1]_t}{k_2[HC_2]_t} \qquad (2)$$

Integrating from t=0 to t=T, the time when the reaction is stopped,

$$\frac{k_1}{k_2} = \frac{\log_{10}[HC_1]_o - \log_{10}[HC_1]}{\log_{10}[HC_2]_o - \log_{10}[HC_2]} \qquad (3)$$

If the nitro derivatives are the only products formed,

$$\frac{k_1}{k_2} = \frac{\log_{10}[HC_1]_o - \log_{10}([HC_1]_o - [N_1])}{\log_{10}[HC_2]_o - \log_{10}([HC_2]_o - [N_2])} \qquad (4)$$

where $[N_1]$, $[N_2]$ are the molar concentrations of the nitro derivatives of HC_1 and HC_2 respectively. Provided that the amount of reaction is small, this assumption will still be valid if other products are formed, provided that the rate of formation of nitro products is not interfered with.

Expanding logarithms and ignoring powers of $\frac{[N]}{c}$, (writing $[HC_1]_o = [HC_2]_o = c$, where $c >> [N_1]$ or $[N_2]$)

$$\frac{k_1}{k_2} \sim \frac{\frac{[N_1]}{c} + \frac{1}{2}\left(\frac{[N_1]}{c}\right)^2 + \frac{1}{3}\left(\frac{[N_1]}{c}\right)^3 + \ldots}{\frac{[N_2]}{c} + \frac{1}{2}\left(\frac{[N_2]}{c}\right)^2 + \frac{1}{3}\left(\frac{[N_2]}{c}\right)^3 + \ldots} \sim \frac{[N_1]}{[N_2]} \qquad (5)$$

Similarly for two positions i and j in the same molecule,

$$\frac{k_i}{k_j} \sim \frac{[N_i]}{[N_j]} \qquad (6)$$

if $[N_i]$ and $[N_j]$ are very small.

2. Calculation of Partial Rate Factors.

In o-xylene, the partial rate factor for the 3-position f_3, is determined as follows:

$$f_3 = \frac{k_{\text{o-xylene}}}{k_{\text{benzene}}} \cdot (\% \text{ 3-isomer}) \cdot \frac{6}{2} \qquad (7)$$

where the first term is the overall rate of nitration of o-xylene relative to benzene and $\frac{6}{2}$ is a statistical factor for the 2 positions of substitution compared with 6 in benzene. The other partial rate factors are determined analogously.

Partial rate factors were determined at 25°, and in order to obtain the best values for the relative rate constants, graphs were plotted of the logarithms of the relative rate constants versus $\frac{1}{T}$, the relative rate constant at 25° being extrapolated from these graphs. In addition, graphs were plotted of $\ln k_i/k_j$ versus $1/T$, where i and j are different positions in the same substrate. From these Arrhenius plots, activation energy differences were estimated:

$$\ln k_i/k_j = -1/RT(\Delta E_i^{\ddagger} - \Delta E_j^{\ddagger}) \qquad (8)$$

where $\Delta E_i^{\ddagger}$ and $\Delta E_j^{\ddagger}$ are the activation energies for substitution at positions i and j respectively.

For a liquid or solid phase reaction,

$$\Delta E_i^{\ddagger} = (\Delta H_o^{\ddagger})_i + RT \qquad (9)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (10)$$

$$\Delta G_i^{\ddagger} = -RT\ln k_i \qquad (11)$$

Thus: $$\Delta\Delta G^{\ddagger} = -RT\ln k_i/k_j \qquad (12)$$

and, $$\Delta\Delta S^{\ddagger} = 1/T(\Delta\Delta E^{\ddagger} - \Delta\Delta G^{\ddagger}) \qquad (13)$$

Hence differences in entropies of activation for two positions in one molecule can be obtained from the Arrhenius

plots.

3. Results

Isomer distributions have been studied in the temperature range 25-100°C for the xylenes and 2,6-dimethylnaphthalene. Competitive nitrations at 25°C between benzene and the xylenes have been carried out in order to determine partial rate factors. For 2,6-dimethylnaphthalene, competitive nitrations were carried out with respect to 2-methyl naphthalene. Nitration of the latter on its own and in competition with naphthalene gave results identical, within experimental error, to those reported by Alcorn and Wells.[130] Competitive nitrations were also carried out on naphthalene with respect to benzene to allow partial rate factors with respect to benzene to be calculated for the mono-methyl- and 2,6-dimethylnaphthalenes.

(i) ortho-xylene

Table (1) shows the variation with temperature of the isomer distribution and relative nitration rate for ortho-xylene. At 25°C the 3-nitro isomer predominates, but as the temperature is increased the proportion of the 4-nitro isomer increases, until at ca. 60°C the two are produced in roughly equal amounts. At higher temperatures the 4-nitro isomer becomes the major product. A plot of the logarithm of the isomer ratio versus $^1/_T$ gives a reasonable straight line (Figure(ii)), from the slope of which an activation energy difference $\Delta E_4^{\ddagger} - \Delta E_3^{\ddagger} = 5.09 \pm 0.34$ Kcals/mole can be

Table 1

Competitive Nitration of o-Xylene and Benzene. Variation of Relative Rate and Isomer Distribution with Temperature.

T°K	Reaction Time (hrs)	ortho-Xylenes (%)		$k_{o\text{-Xylene}}/k_{Benzene}$	$\ln k_{o\text{-Xylene}}/k_{Benzene}$	$\ln [3\text{-}NO_2]/[4\text{-}NO_2]$	$\frac{1}{T} \times 10^3$
		$3\text{-}NO_2$	$4\text{-}NO_2$				
298.0	198	72.7±4.4	27.3±1.7	30.9 ±2.4	3.43±0.08	0.982±0.083	3.356
313.0	96	63.6±1.3	36.4±0.7			0.560±0.028	3.195
324.0	48	56.9±1.8	43.1±1.4	10.7 ±0.5	2.37±0.05	0.278±0.044	3.086
333.0	30	51.7±1.0	48.3±1.0	7.9 ±1.1	2.07±0.13	0.068±0.027	3.003
343.0	17	46.2±1.5	53.8±1.8	6.63±0.08	1.89±0.01	-0.151±0.045	2.915
352.0	10	41.5±2.4	58.5±3.5	5.18±0.31	1.65±0.06	-0.343±0.080	2.841
362.0	9			3.2 ±0.3	1.16±0.02		2.762
373.0	4	37.9±1.3	62.1±2.2	2.58±0.27	0.95±0.10	-0.494±0.048	2.681

evaluated. The large errors involved make a detailed interpretation of the entropy difference unjustified, but qualitatively it can be seen that for 3-substitution adjacent to a methyl group, relative to the unhindered 4-position, there is a significant entropy difference. ($\Delta S_4^{\ddagger} - \Delta S_3^{\ddagger} = 15.2 \pm 1.2$ entropy units)

The plot of the logarithm of the overall rate ratio against 1/T gives a reasonable straight line (Figure(i)), from which the relative rate at 25°C can be better evaluated as 28.2±3.8. From figure(ii) the isomer ratio is estimated as:

$$\frac{[\text{3-nitro-o-xylene}]}{[\text{4-nitro-o-xylene}]} = 2.64 \pm 0.13$$

at 25°C, giving:

$$\%\text{3-nitro-o-xylene} = 72.5 \pm 3.6$$

$$\%\text{4-nitro-o-xylene} = 27.5 \pm 1.4$$

Thus partial rate factors for the 3 and 4 positions in o-xylene may be calculated as 61.4±8.8 and 23.3±3.3 respectively.

(ii) <u>para-xylene</u>

Table (2) shows the variation with temp. of the relative nitration rate of p-xylene relative to benzene. A plot of the logarithm of the relative rate versus 1/T gives a fairly good straight line (Figure(iii)), from which the relative rate at 25°C is extrapolated as 36.6± 4.9. Thus the partial rate factor at 25°C for p-xylene is 54.9±7.3.

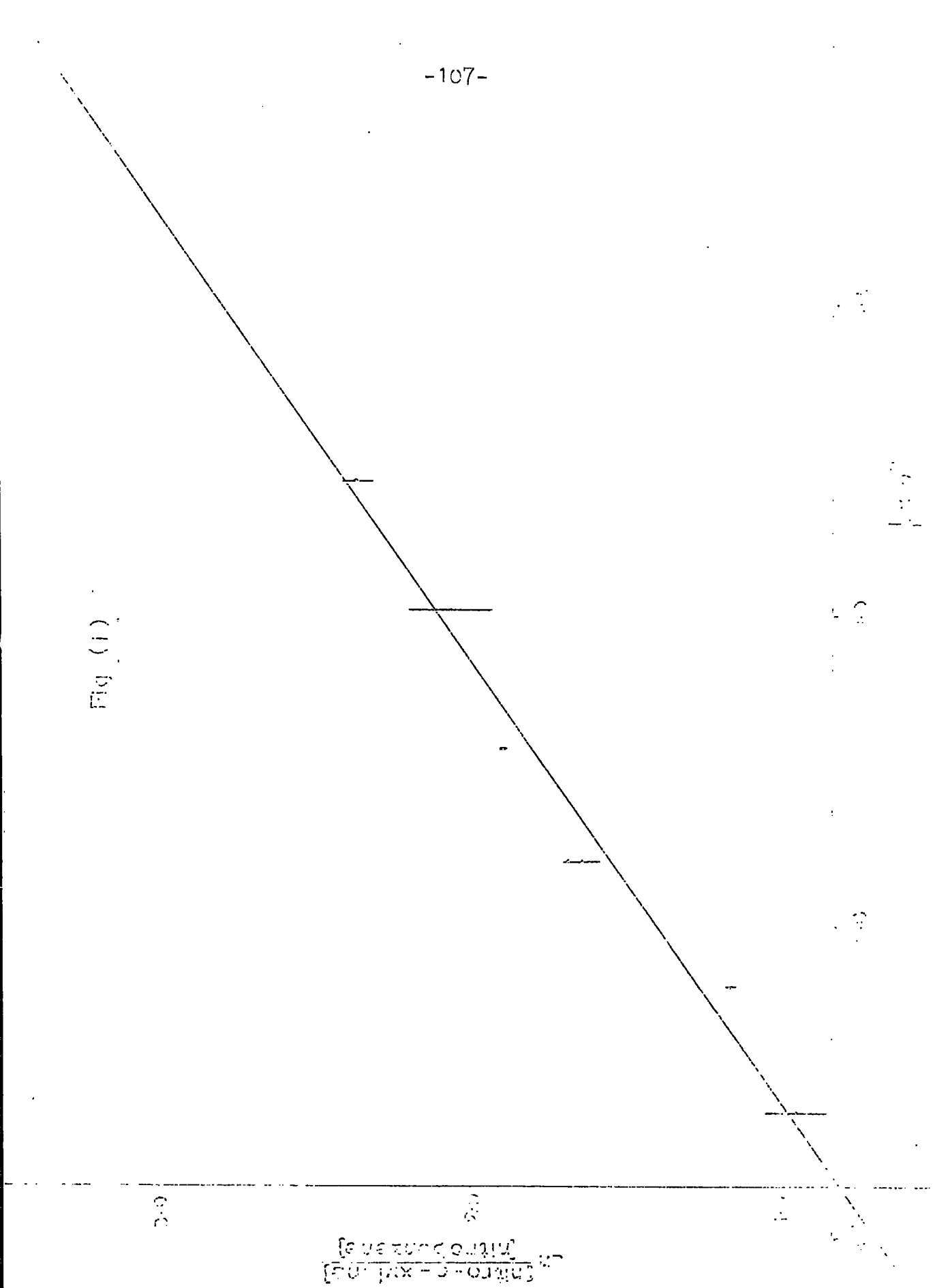


Fig. (1)

Table 2

Competitive Nitration of p-Xylene and Benzene. Variation of Relative Rate with Temperature.

$T^{\circ}K$	Reaction Time(hrs)	Nitrobenzene %	Nitro-p-Xylene %	$\frac{k_{p\text{-Xylene}}}{k_{Benzene}}$	$\ln\frac{k_{p\text{-Xylene}}}{k_{Benzene}}$	$\frac{1}{T}\times10^{3}$
313.0	72	4.47±0.04	95.5±0.9	21.4±0.3	3.06±0.01	3.195
324.0	24	5.85±0.13	94.2±2.1	16.1±0.5	2.78±0.03	3.086
333.0	34	7.41±0.16	92.6±2.0	12.5±0.4	2.53±0.03	3.003
342.5	16	8.70±0.32	91.3±3.4	10.5±0.9	2.35±0.08	2.920
349.5	3	8.00±0.10	92.0±1.1	11.5±0.2	2.44±0.02	2.861
363.0	2	14.18±0.15	85.8±0.8	6.1±0.1	1.80±0.02	2.755
381.0	1.5	20.83±0.23	79.2±1.1	3.8±0.2	1.34±0.02	2.625

(iii) meta-xylene

Table (3) shows the variation with temp. of the isomer distribution and relative nitration rate for m-xylene. Only two isomers were detected in the temp. range 25-100°C. From a plot of the logarithm of the isomer ratio against 1/T, (Figure(iv)), an activation energy difference $\Delta E_2^{\ddagger} - \Delta E_4^{\ddagger}$ = 1.15±0.16 Kcals/mole can be evaluated. There are large errors associated with the calculation of the entropy differences (0.27±0.04 e.u.), but it can be seen that the difference is small. The isomer ratio at 25°C is evaluated as:

$$\frac{[4\text{-nitro-m-xylene}]}{[2\text{-nitro-m-xylene}]} = 7.93 \pm 0.33$$

from which the isomer proportions are:

$$\%\text{4-nitro-m-xylene} = 88.8 \pm 3.7$$

$$\%\text{2-nitro-m-xylene} = 11.2 \pm 0.5$$

A corresponding plot of the logarithm of the relative rate against 1/T gives a straight line (Figure(v)), from which the relative rate at 25°C is evaluated as 399±48. The partial rate factors of the 4 and 2 positions in m-xylene may be calculated as 1063±135 and 268±34 respectively.

(iv) Naphthalene

Table (4) shows the variation with temp. of the isomer distribution and the relative nitration rate for naphthalene. The predominance of the 1-nitro isomer is largely due to the lower activation energy $\Delta E_1^{\ddagger} - \Delta E_2^{\ddagger} = -(1.49 \pm 0.28)$ Kcals/mole. The difference in the entropy of activation,

Table 3

Competitive Nitration of m-Xylene and Benzene. Variation of Relative Rate and Isomer Distribution with Temperature.

T°K	Reaction Time (hrs)	meta-Xylenes (%)		$k_{m\text{-Xylene}}/k_{Benzene}$	$\ln k_{m\text{-Xylene}}/k_{Benzene}$	$\ln [4\text{-}NO_2]/[2\text{-}NO_2]$	$\frac{1}{T} \times 10^3$
		4-NO_2	2-NO_2				
298.0	168	89.0±0.9	11.0±0.8	454±46	6.11±0.09	2.07±0.03	3.356
313.0	96	88.6±2.5	11.36±0.32	212±38	5.36±0.16	2.05±0.04	3.195
323.0	72	87.2±0.2	12.79±0.03	128± 1	4.85±0.02	1.92±0.01	3.096
333.0	34	86.3±1.9	13.66±0.30	83.4±0.9	4.42±0.01	1.84±0.03	3.003
343.0	16	85.9±0.7	14.14±0.11	65.0±2.0	4.17±0.03	1.80±0.01	2.915
353.0	10	85.3±0.5	14.68±0.09			1.76±0.01	2.833
363.0	5	84.8±0.8	15.15±0.15	31.5±3.3	3.45±0.10	1.72±0.02	2.755
373.0	3	84.1±1.7	15.85±0.32	24.2±3.2	3.19±0.12	1.67±0.03	2.681

Fig (iv)

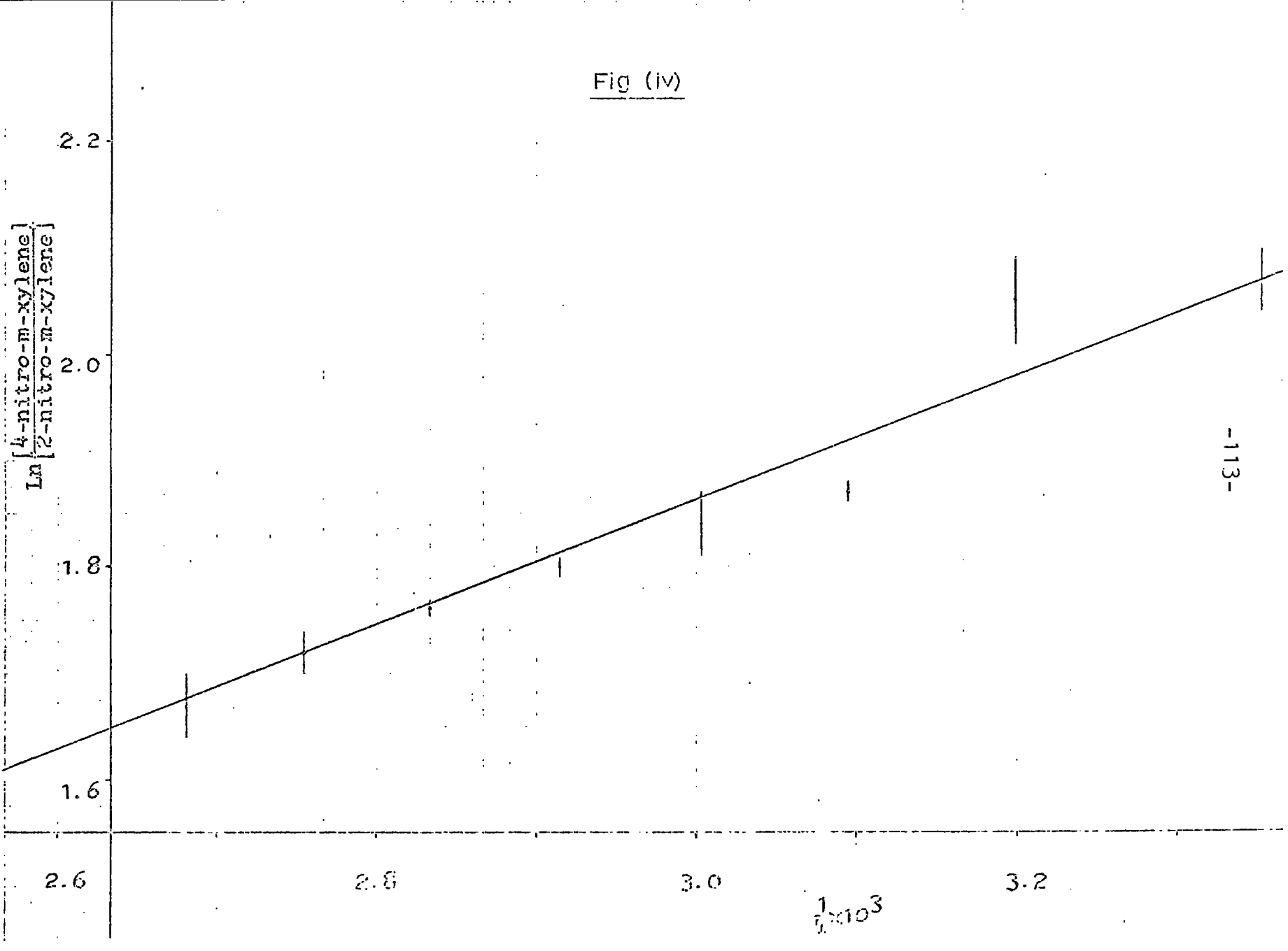

2.2
2.0
1.8
1.6
Ln [4-nitro-m-xylene] / [2-nitro-m-xylene]
2.6
2.8
3.0
3.2
1/T x10^3

Table 4

Competitive Nitration of Naphthalene and Benzene. Variation of Relative Rate and Isomer Distribution with Temperature.

T°K	Reaction Time (hrs)	Naphthalenes (%)		$k_{naphth.}/k_{benzene}$	$\ln k_{naphth.}/k_{benzene}$	$\ln [1\text{-}NO_2]/[2\text{-}NO_2]$	$\frac{1}{T} \times 10^3$
		1 -NO_2	2 -NO_2				
298.0	198	94.7±6.7	5.28±0.37	165 ±20	5.11±0.11	2.89±0.10	3.356
313.0	96	94.3±1.6	5.71±0.10	95 ± 8	4.55±0.10	2.80±0.08	3.195
323.0	48	93.8±4.7	6.25±0.30	73.8± 1.3	4.30±0.02	2.71±0.06	3.096
333.0	34	93.6±4.2	6.54±0.29			2.66±0.06	3.003
342.5	17	93.1±1.5	6.90±0.11	44.8± 1.1	3.80±0.02	2.60±0.02	2.920
373.0	0.5	91.8±4.6	8.20±0.41	23.1± 2.4	3.14±0.10	2.42±0.07	2.681

$\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger} = 0.0 \pm 0.5$ e.u., but the substantial error does not justify any rigorous conclusions. These values are obtained from the plot of the logarithms of the isomer ratios versus 1/T, (Figure(vi)), from which the isomer ratio at 25°C is obtained as:

$$\frac{[1\text{-nitro-naphthalene}]}{[2\text{-nitro-naphthalene}]} = 18.6 \pm 0.6$$

giving the isomer percentages:

$$\%1\text{-nitro-naphthalene} = 94.9 \pm 3.1$$

$$\%2\text{-nitro-naphthalene} = 5.1 \pm 0.2$$

The results are in good agreement with those previously reported by Alcorn and Wells(at 25°C)[138] and Streitwieser and Fahey(50, 100 °C)[139]. From the plot of the logarithm of the relative nitration rate versus 1/T, (Figure(vii)), the relative rate at 25°C is obtained as 149 ± 15, and from the above isomer distribution, partial rate factors of 212 ± 22 and 11.4 ± 1.2 may be calculated for the 1 and 2 positions respectively.

(v) 2,6-dimethylnaphthalene

In the nitration of 2,6-dimethylnaphthalene, all of the 3 possible isomers were obtained, and Table (5) shows the variation of the isomer distribution with temp. From plots of the logarithms of the isomer ratios versus 1/T, (Figures (viii) and (ix)), activation energy differences $\Delta E_4^{\ddagger} - \Delta E_1^{\ddagger} = 0.83 \pm 0.08$ Kcals/mole and $\Delta E_3^{\ddagger} - \Delta E_4^{\ddagger} = 2.92 \pm 0.40$ Kcals/mole can be evaluated. The corresponding entropy

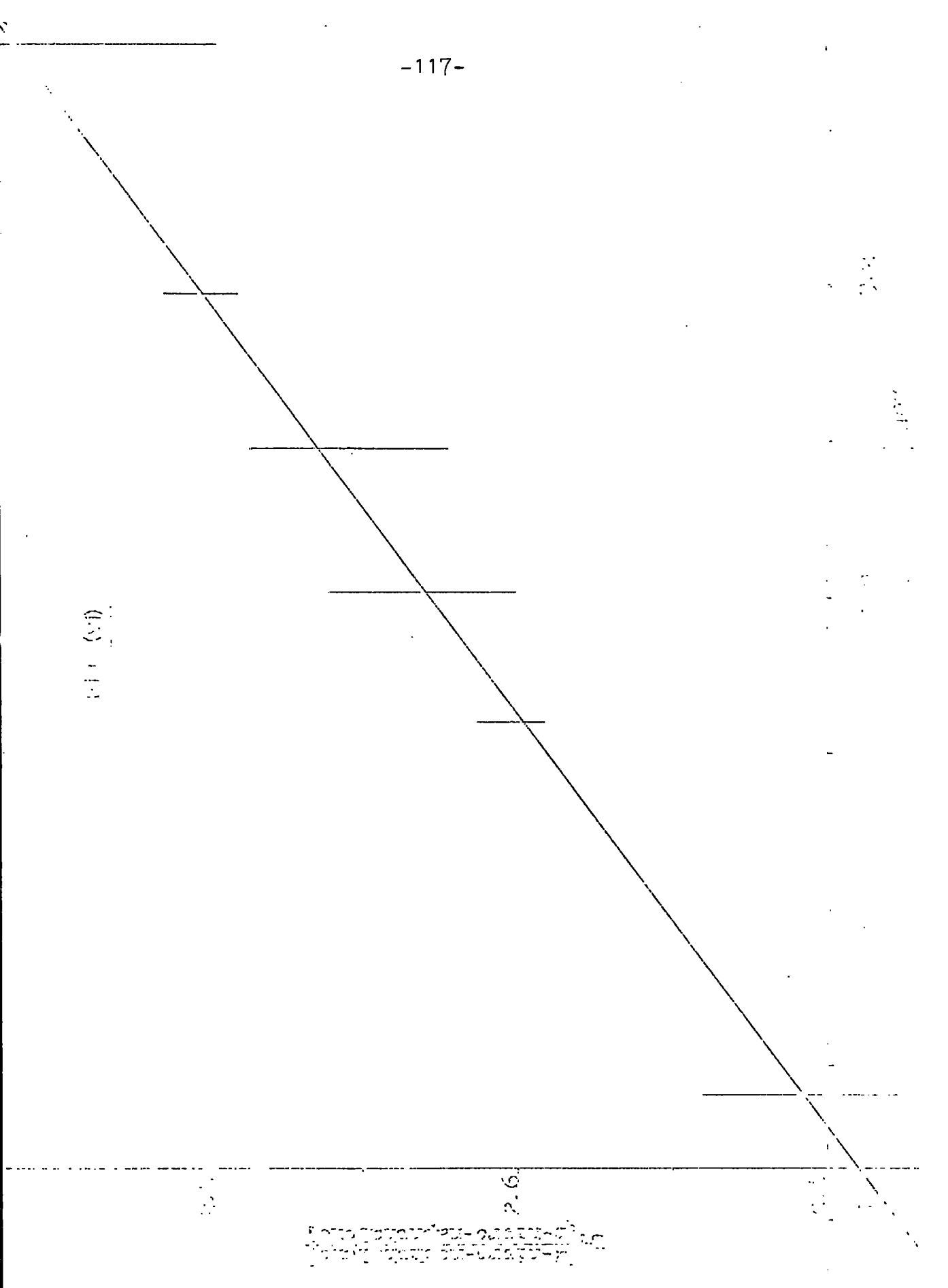
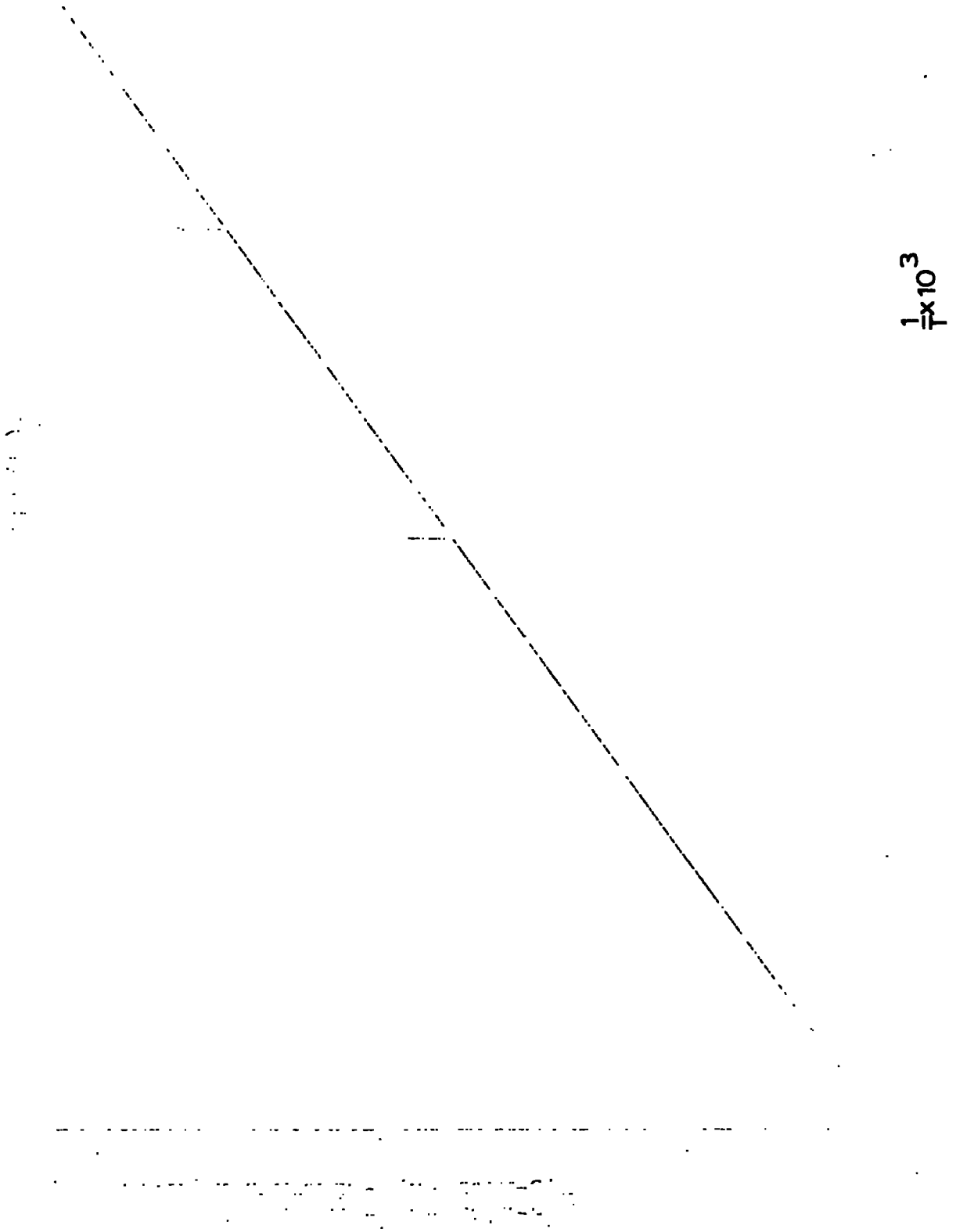


Table 5

The Nitration of 2,6-Dimethylnaphthalenes. Variation of Isomer Distribution with Temperature.

T°K	Reaction Time (hrs)	2,6-Dimethylnaphthalenes (%)			$\ln \frac{[1\text{-}NO_2]}{[4\text{-}NO_2]}$	$\ln \frac{[4\text{-}NO_2]}{[3\text{-}NO_2]}$	$\frac{1}{T} \times 10^3$
		1-NO_2	4-NO_2	3-NO_2			
273.0	24	82.4±0.8	17.1±0.2	0.43±0.02	1.57±0.01	3.68±0.04	3.663
298.0	24	80.8±1.8	18.5±0.4	0.70±0.03	1.47±0.02	3.31±0.04	3.356
323.0	11	78.6±0.8	20.3±0.3	1.08±0.03	1.35±0.02	2.93±0.03	3.096
343.0	5	75.7±0.2	21.2±0.1	3.0 ±1.3	1.27±0.01	1.96±0.57	2.915
378.0	2	74.4±0.3	23.0±0.1	2.6 ±0.1	1.18±0.01	2.18±0.03	2.646


$\frac{1}{T} \times 10^3$

differences are $\Delta S^{\ddagger}_1 - \Delta S^{\ddagger}_4 = 0.17 \pm 0.02$ e.u. and $\Delta S^{\ddagger}_3 - \Delta S^{\ddagger}_4 = 3.2 \pm 0.5$ e.u., though again the errors are rather large.

The competitive nitration between 2,6-dimethylnaphthalene and 2-methylnaphthalene at 25°C gave a relative rate ratio of 9.9 ± 0.3. The competitive nitration between 2-methylnaphthalene and naphthalene reproduced, within experimental error, the results of Alcorn and Wells. Using their results,[138] and the isomer distributions in Table 5, the partial rate factors for 2,6-dimethylnaphthalene, relative to naphthalene, were evaluated as 436 ± 148, 148 ± 71, and 100.1 ± 36.6 for the 1, 3 and 4 positions respectively.

4. Discussion

A quantitative discussion of the above results will be given in a later chapter, but it is of interest to compare them qualitatively with other experimental data.

Figure 1 shows a plot of the relative reactivities in nitration at 25°C, as logarithms, against the logarithms of the relative equilibrium constants for protonation in HF. The nitration data for toluene and the monomethylnaphthalenes are taken from references(137) and (138), while the equilibrium constants are from reference(57). The results are fairly good, the graph being a straight line through the origin. A reactivity constant σ_r and reaction constant ρ^* may be defined by:

$$\log k_r/k_{benzene} = \sigma_r \rho^*$$

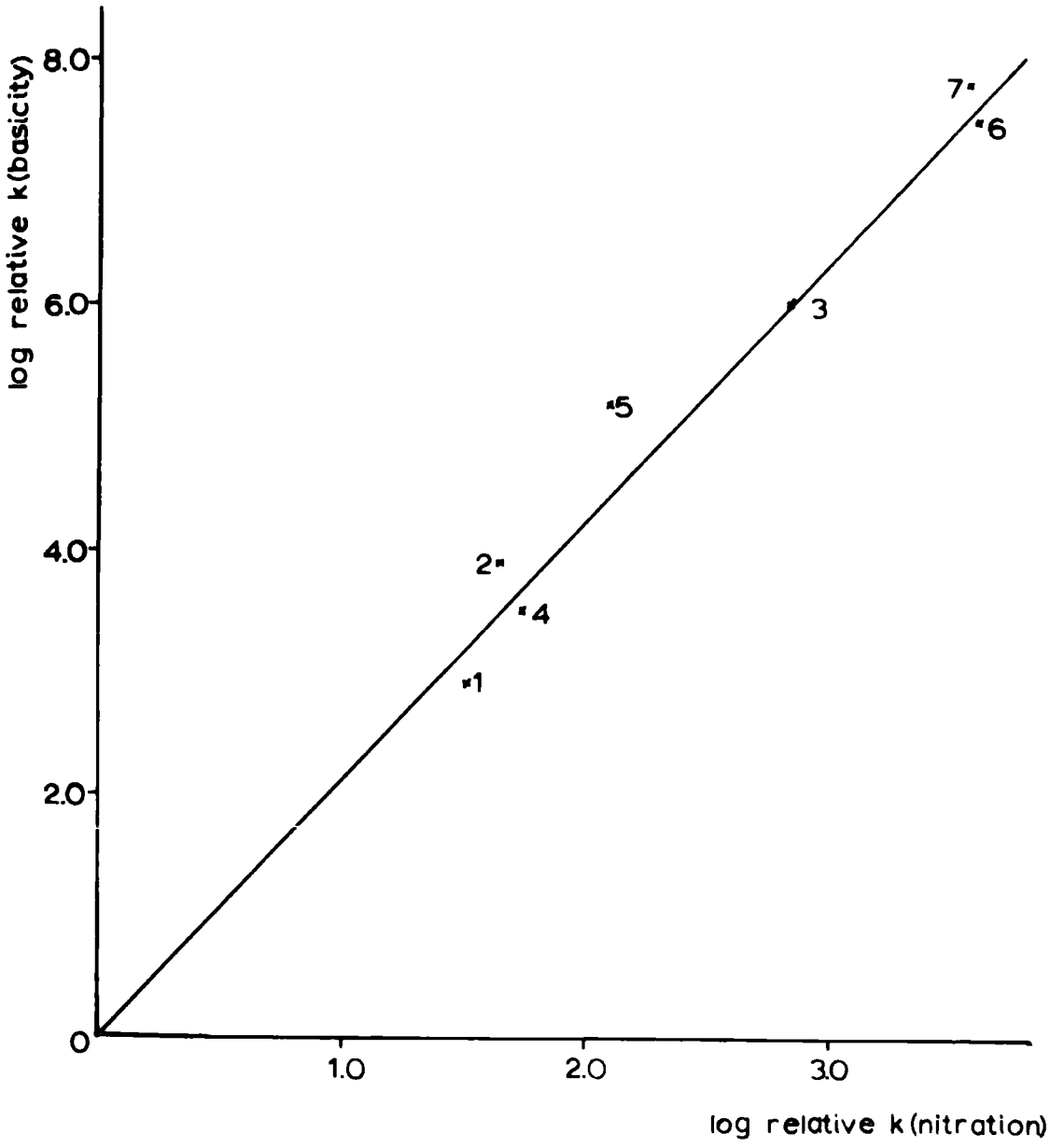

log relative k(basicity)
8.0
6.0
4.0
2.0
0
1.0
2.0
3.0
log relative k(nitration)
1
2
3
4
5
6
7

Figure 1.

where the standard electrophilic substitution ρ^* is unity, for the protonation reaction. From Figure 1, ρ^* for nitration in nitric/acetic acid media at 25°C is evaluated as 0.48. From published data for the methylbenzenes for protodedeuteration in CF_3COOH-H_2SO_4-CCl_4 media[140] and chlorination in acetic acid,[141] ρ^* can be calculated as 0.83 and 1.33 respectively. This indicates the much lower selectivity of the electrophile in nitration in acetic/nitric acid media compared with the other reactions.

The partial rate factors for the xylenes, naphthalene and 2,6-dimethylnaphthalene are shown in Figure 2 with previously published data for toluene[137] and the monomethylnaphthalenes.[138] Comparable studies have been reported for protonation equilibria in HF,[57, 140] involving particular sites in a molecule, and protodetritiation[141, 142] in trifluoroacetic acid media at 70°. Figure 3 shows a plot of log k (partial rate factor for nitration) versus log relative K (equilibrium protonation). The graph is a good straight line and suggests that there should be a reasonable correlation between the log k's and localisation energies. The corresponding plot of partial rate factors for nitration and protodetritiation is shown in Figure 4. Here there is a considerable spread, with the 2-position in m-xylene and the 4-position in o-xylene showing the greatest deviation from a linear correlation. For the former there

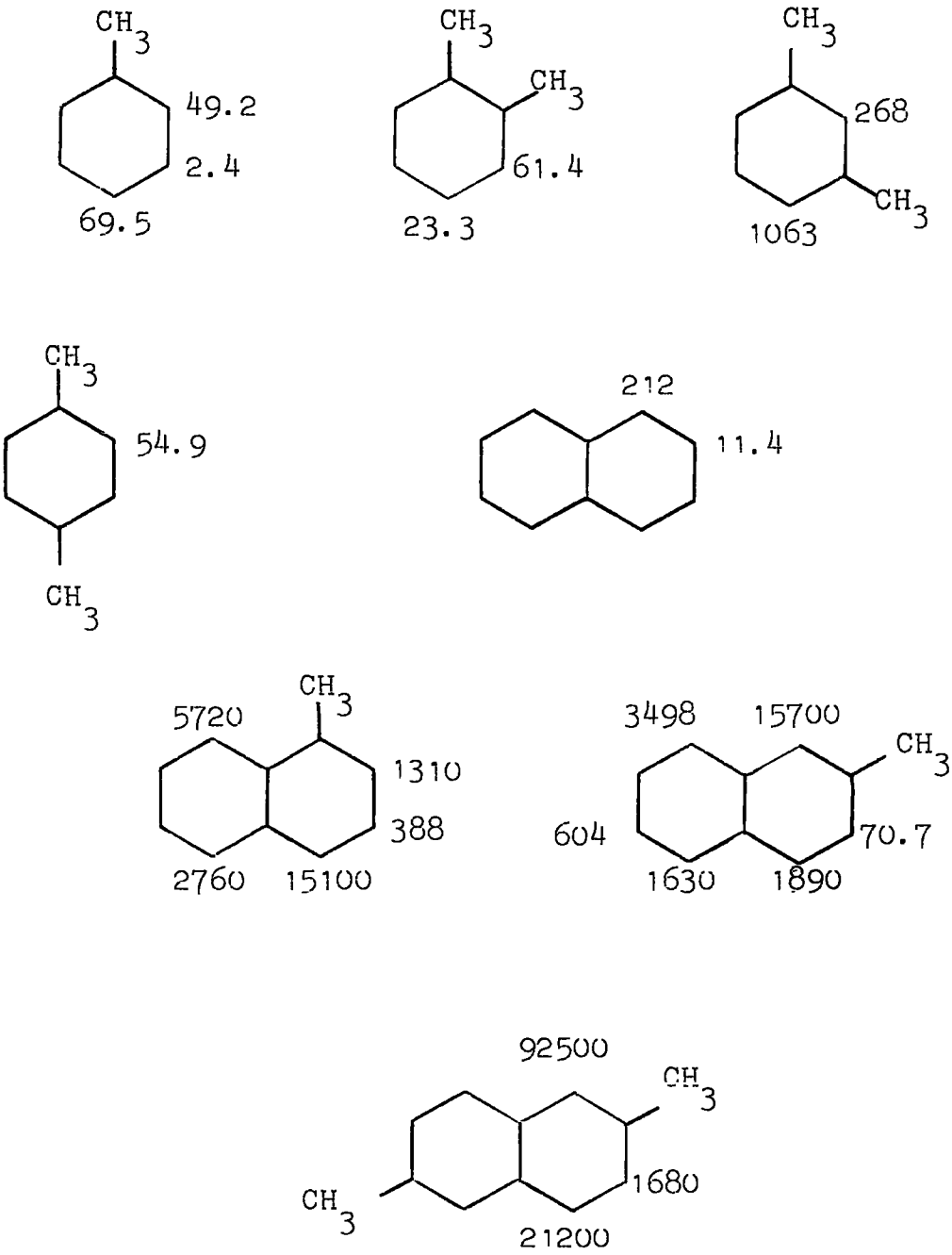


Figure 2

Partial Rate Factors Relative to Benzene at 25°C

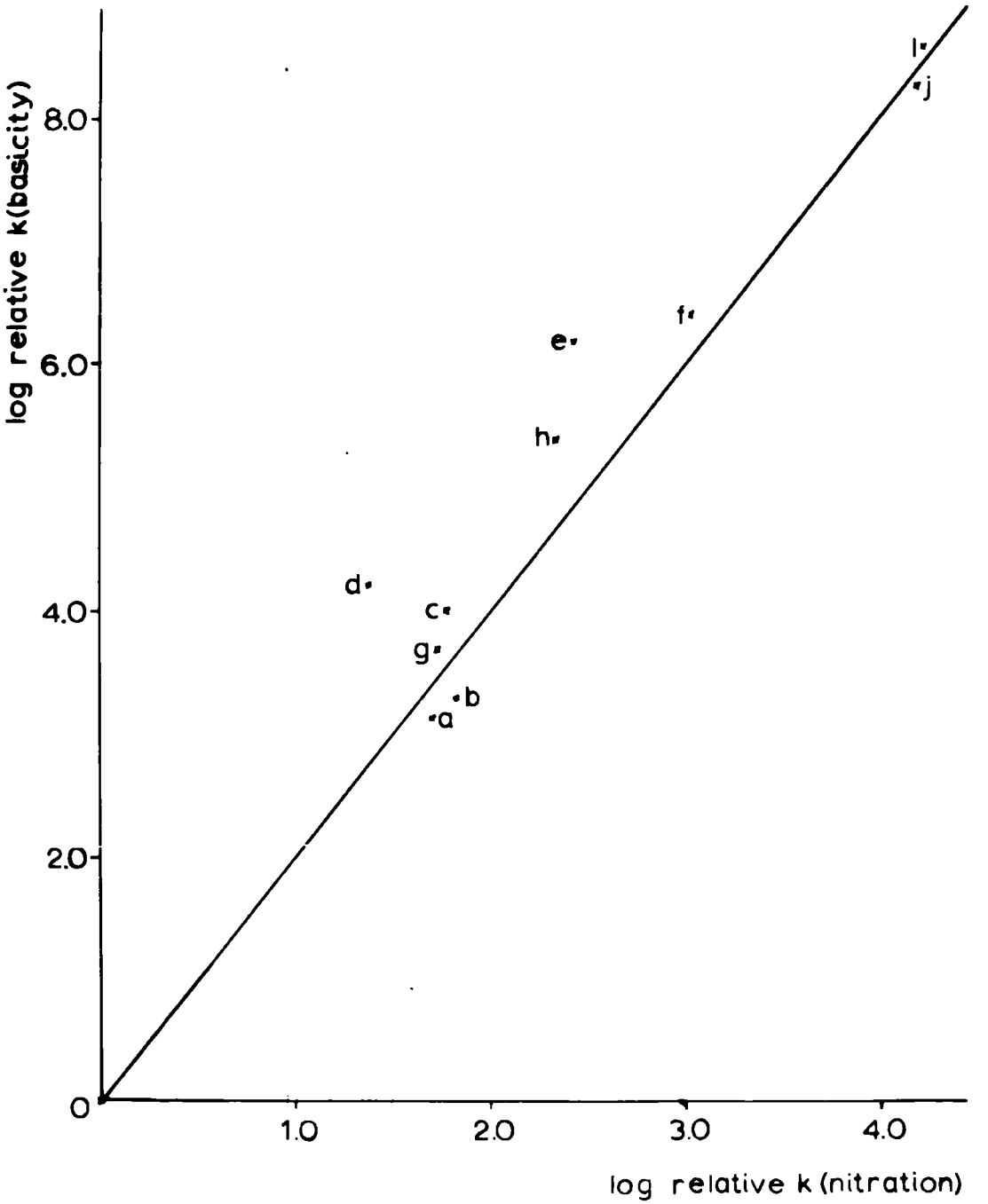

log relative k(basicity)
8.0
6.0
4.0
2.0
0
1.0
2.0
3.0
4.0
log relative k (nitration)
a
b
c
d
e
f
g
h
i
j

Figure 3.

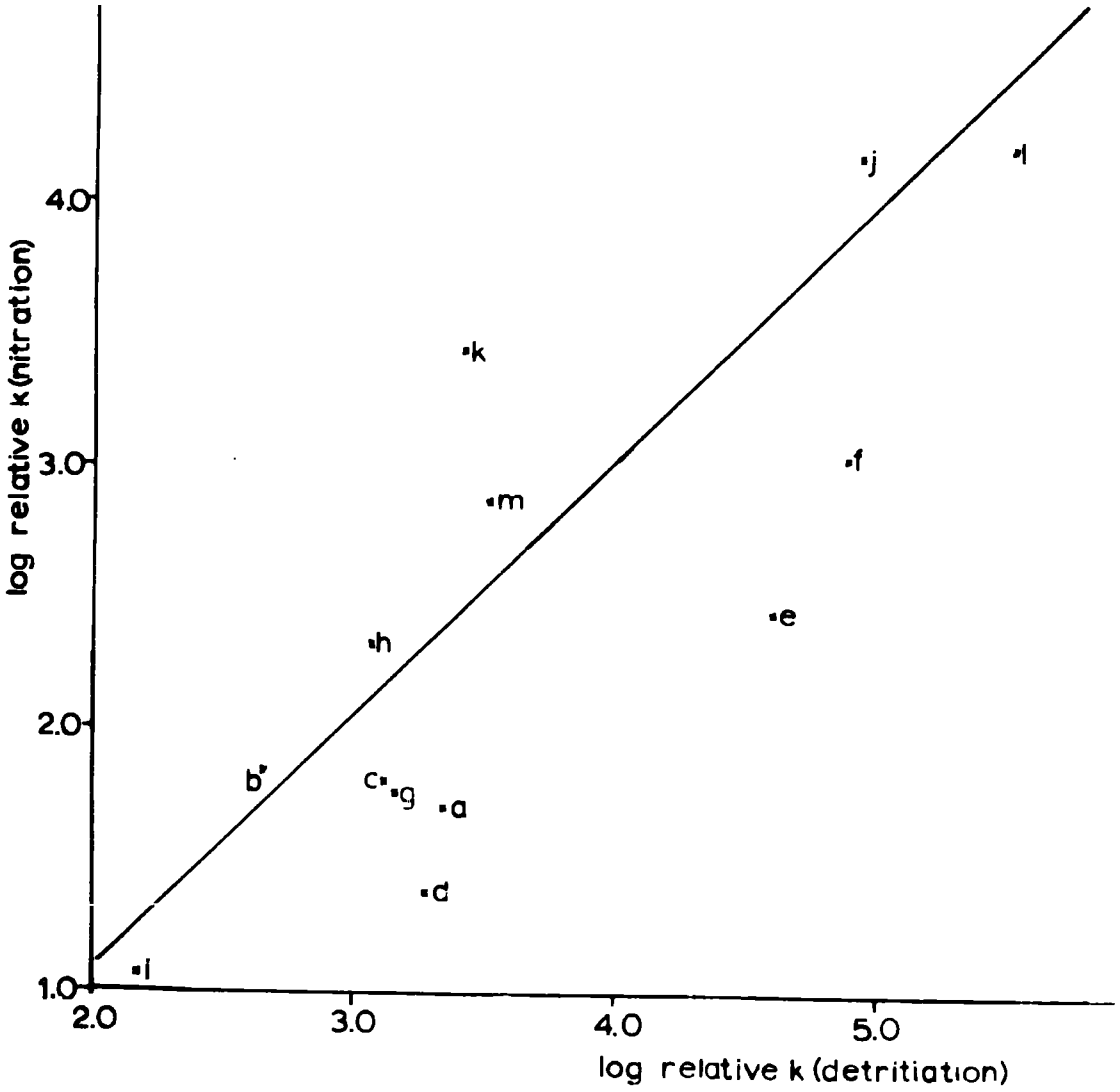

log relative k (nitration)
4.0
3.0
2.0
1.0
2.0
3.0
4.0
5.0
log relative k (detritiation)
a
b
c
d
e
f
g
h
i
j
k
l
m

Figure 4.

is a steric effect, and the anomalous behaviour of the latter in nitration, is also shown to a lesser extent in protodetritiation.

At present there are no partial rate factor data to compare with the results for the nitration of 2,6-dimethylnaphthalene, but it is of interest to compare the rate enhancement produced in one ring by methyl substitution in the other. Thus, for 2-methylnaphthalene, the rate enhancement at the 5 and 8 positions with respect to naphthalene is 7.7 and 16.5 respectively. For 2,6-dimethylnaphthalene with respect to 2-methylnaphthalene, the corresponding figures are 5.89 and 11.25 respectively. The rate enhancement at the 3 position is 23.8, but there are no figures available for the corresponding 7 position in 2-methylnaphthalene.

Key for Figures 1, 3 and 4.

1 Toluene	a Toluene-2-position
2 o-xylene	b Toluene-4-position
3 m-xylene	c o-xylene-3-position
4 p-xylene	d o-xylene-4-position
5 Naphthalene	e m-xylene-2-position
6 1-Me-naphthalene	f m-xylene-4-position
7 2-Me-naphthalene	g p-xylene-2-position
h Naphthalene-1-position	i naphthalene-2-position
j 1-Me-naphthalene-4-position	k 1-Me-naphthalene-5-position
l 2-Me-naphthalene-1-position	m 2-Me-naphthalene-3-position

5. Experimental

Materials

Nitric Acid

Nitric acid (10 ml., d=1.51) was mixed with sulphuric acid (10 ml, d=1.84) and distilled (room temperature, 0.001 mm) into a liquid air cooled flask containing sulphuric acid (5 ml, d=1.84). Nitric acid was distilled from this receiver (room temperature, 0.001 mm) into a liquid air cooled flask containing glacial acetic acid (1 ml), until 0.63 g had been transferred. The colourless solution of nitric acid in acetic acid thus obtained was allowed to melt and immediately added to the solution to be nitrated.

Acetic acid and Benzene

British Drug Houses ANALAR acetic acid and benzene were used without further purification.

o-Xylene, m-xylene and p-xylene were dried before use with phosphorus pentoxide, and distilled. (They were shown to be pure by gas chromatography.)

Naphthalene, m.p. 80.5-81.0°, 2-methylnaphthalene, m.p. 31.5°, and 2,6-dimethylnaphthalene, m.p. 110-111°, (pure, gas chromatography) were used without further purification.

Analytical Nitrations

The nitrations were conducted in a thermostat controlled by a Jumo contact thermometer with temperature control $\pm$0.01°. The reaction mixtures were stirred ca. 1200 rpm and the amounts of substrate (o-, m-, p-xylene or naphthalene

alone or with benzene; 2,6-dimethylnaphthalene alone or with 2-methylnaphthalene) were each 0.01 mole. The substrates were dissolved in acetic acid (25 ml) and allowed to equilibrate at the required temperature before treating with a solution of nitric acid (0.63 g, 0.01 mole) in acetic acid (1 ml), prepared as above. The reaction mixture was left until colouration (yellow, orange or red, depending on substrate) showed that some nitration had occurred. In competitive nitrations less than 5% reaction was allowed to take place, so that partial rate factor calculations would be valid.

Preparation of Samples for Analysis

The reaction mixtures were quenched by pouring into ice-water (200 ml) with stirring. The suspensions were neutralised with sodium carbonate before extraction with ether (4x100 ml). The ether extracts were washed with water (2x100 ml) and these washings were extracted with ether (50 ml). The combined ether extracts were dried ($MgSO_4$), filtered, and the magnesium sulphate residue washed with ether (30ml). The total ether solutions were distilled, and the cooled residual oil dissolved in a small amount of chloroform.

This procedure was checked with standard solutions of reaction products. Within the limits of experimental error of the gas chromatographic analyses, the compositions before and after extraction were the same.

Preparative Reactions

Preparative nitrations were carried out on each hydrocarbon using the same experimental procedure as above. A larger amount of substrate was used, with the temperature maintained at 100° for 4hr.

Gas Chromatography

All analyses were made with a single column Pye 104 gas chromatograph fitted with a flame ionisation detector. This was coupled to a Honeywell-Brown recorder (-1 to +10 mV) fitted with a Kent Chromalog integrator.

The columns employed for the analyses were:

a) 5% neo-pentylglycol adipate on Celite (90-100 mesh), 5 feet by 1/16 in. i.d.

b) 10% methyl silicone rubber gum on Celite (90-100 mesh), 10 feet by 1/16 in. i.d.

Nitrogen was used as carrier gas at a flow-rate of 60 ml/min.

The detector was calibrated for all the products of the reactions studied except 3-nitro-2,6-dimethylnaphthalene, and the minor isomers of nitrated 2-methylnaphthalene. For all the nitro isomers tested, the weight responces were identical, for each particular hydrocarbon, to within 1%, and linear over the range 0.1-10 μl sample injected. Results for the compounds not tested are therefore quoted with confidence. Peak areas, measured with the integrator or from the recorder trace with a planimeter,

were multiplied by the appropriate correction factor for molecular weight differences and the difference in response for nitro isomers of different hydrocarbons. Isomer distributions were recorded as product ratios and the standard deviations estimated from a minimum of three analyses. These figures were then converted into Napierian logarithms for the Arrhenius plots, as in tables 1-5.

Identification of Products from Analytical Reactions

p-Xylene was mono-nitrated by the method of Kobe and Levin.[143] The nitro-p-xylene formed was distilled at 150° (45 mm) using a 12 in. Vigreux column with a high reflux ratio. The glc retention time and infra red spectrum of this sample were identical to those of the product from the preparative nitration of p-xylene, carried out under the conditions of the analytical runs. The infra red spectrum showed an intense absorption at 1351 cm^{-1}, characteristic of the symmetrical stretching absorption frequency of the nitro group in nitro-p-xylene.[144]

Nitro-o-xylenes

From the preparative nitration of o-xylene, two products were separated on a Pye 105 preparative scale gas chromatograph, using a 30 ft.x1/8 in. i.d. column packed with 25% Apiezon L on Celite (60-72 mesh) at 200°. Of these, 3-nitro-o-xylene was identified by its infra red spectrum and glc retention time, which were identical to those of an authentic sample. Careful recrystallisation of the sec-

ond product from absolute ethanol gave yellow needles, m.p. 26-28°. (4-nitro-o-xylene, m.p. 27.6-28.7°[145]) (Found: C, 63.7; H, 6.2. Calc. for $C_8H_9NO_2$: C, 63.5; H, 6.0%)

Nitro-m-xylenes

Two products from the preparative nitration of m-xylene were separated on the Pye 105 gas chromatograph. These were identified as 2-nitro and 4-nitro-m-xylenes by comparison of their infra red spectra and glc retention times with those of authentic samples.

Nitronaphthalenes

Two products from the preparative nitration of naphthalene were separated on the Pye 105 gas chromatograph (25% Methyl silicone rubber gum on Celite (60-72 mesh), 30 ft. x 1/8 in. i.d.) at 250°. Of these, 1-nitronaphthalene was characterised by comparison of its infra red spectrum, glc retention time, and m.p. (57-58°), with those of an authentic sample. The second product, after recrystallisation from ethanol, gave yellow needles, m.p. 77-78°. (lit: [146] 2-nitronaphthalene, m.p. 77.5-78.2°) (Found: C, 69.2; H, 4.0; Calc. for $C_{10}H_7NO_2$: C, 69.3; H, 4.1%).

Nitro-2-methylnaphthalenes

2-Methynaphthalene (7.1 g) was nitrated by the method of Fierz-David and Mannhart[147]. The 1-nitro-2-methylnaphthalene obtained (6.2 g) crystallised from ethanol as orange needles, m.p. 80-82°. (lit: 80-81°) The product from the preparative nitration of 2-methylnaphthalene, carried

out under the conditions of the analytical runs, was eluted down an 18x3/4 in. i.d. column packed with alumina (Camag, Brockmann activity 1), using carbon tetrachloride as eluent. One fraction was obtained pure with the same glc retention time and infra red spectrum as the authentic sample of 1-nitro-2-methylnaphthalene, prepared as above. The peak areas for the other isomers agreed, within experimental error, with the isomer proportions published by Alcorn and Wells.[138] (although these peaks were not characterised) In the competitive nitration between 2-methyl and 2,6-dimethyl-naphthalenes, the glc peak for 1-nitro-2-methylnaphthalene was identified, and the proportions of the other isomers were interpolated from the data of Alcorn and Wells.

Nitro-2,6-dimethylnaphthalenes

The product from the preparative scale nitration of 2,6-dimethylnaphthalene was eluted down an 18x3/4 in. column packed with alumina (Camag, Brockmann activity 1), using petroleum ether (b.p. 40-60°). Two fractions were obtained, which were purified further by thin-layer chromatography using Kieselgel as stationary phase and cyclohexane as eluent. After crystallisation from ethanol, the two fractions had m.p.'s 66.0-66.5° and 78-79°. (lit: 1-nitro-2,6-dimethylnaphthalene, 68°[148], 4-nitro-2,6-dimethylnaphthalene, 84-85°[149]) Glc analysis of the fraction with m.p. 66-66.5° showed ca. 1% of a second isomer, which had been

detected in the analytical runs. It seemed reasonable to assign this as 3-nitro-2,6-dimethylnaphthalene, although all attempts to separate it failed. The identities of the other two isomers were established unambiguously by means of their n.m.r. spectra.

2,6-Dimethyl-1-nitronaphthalene

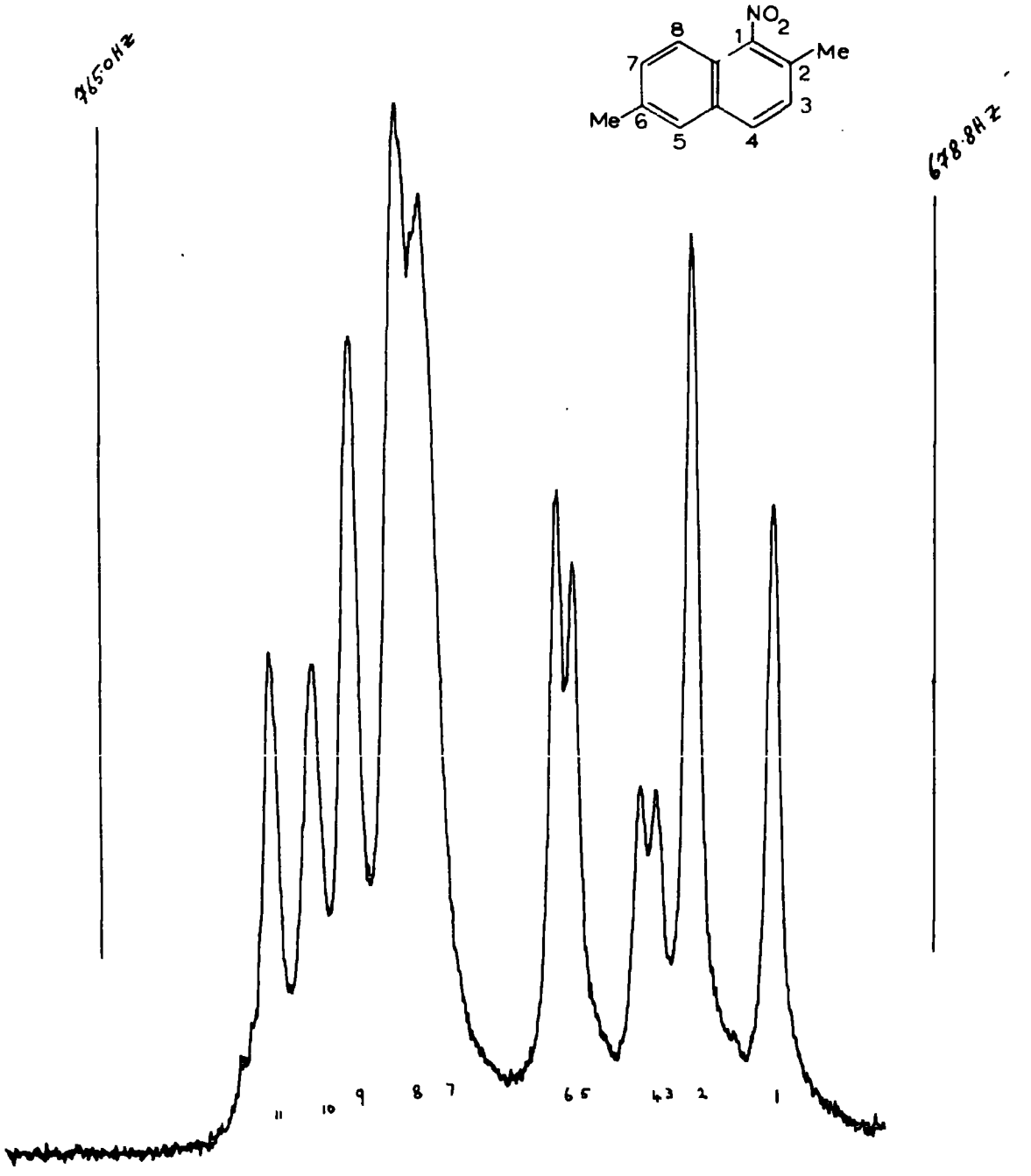
Spectrum (a) shows the low field aromatic region of the n.m.r. spectrum of 2,6-dimethyl-1-nitronaphthalene(in carbon tetrachloride), with a sweep width of 250Hz at 100 MHz. The methyl groups (not shown) form a doublet at ↑7.72 and 7.68ppm., in agreement with Wells[173] who observed a doublet with spacing 0.04ppm. Protons 3 and 4 form an AB quartet (peaks 1,2,9 and 11). Using the INDOR double resonance technique, the following assignment was made.[172,174]

Peaks	Proton	Peaks	Proton
1, 2	3	7	5
3, 4, 5, 6	7	8, 10	8
		9, 11	4

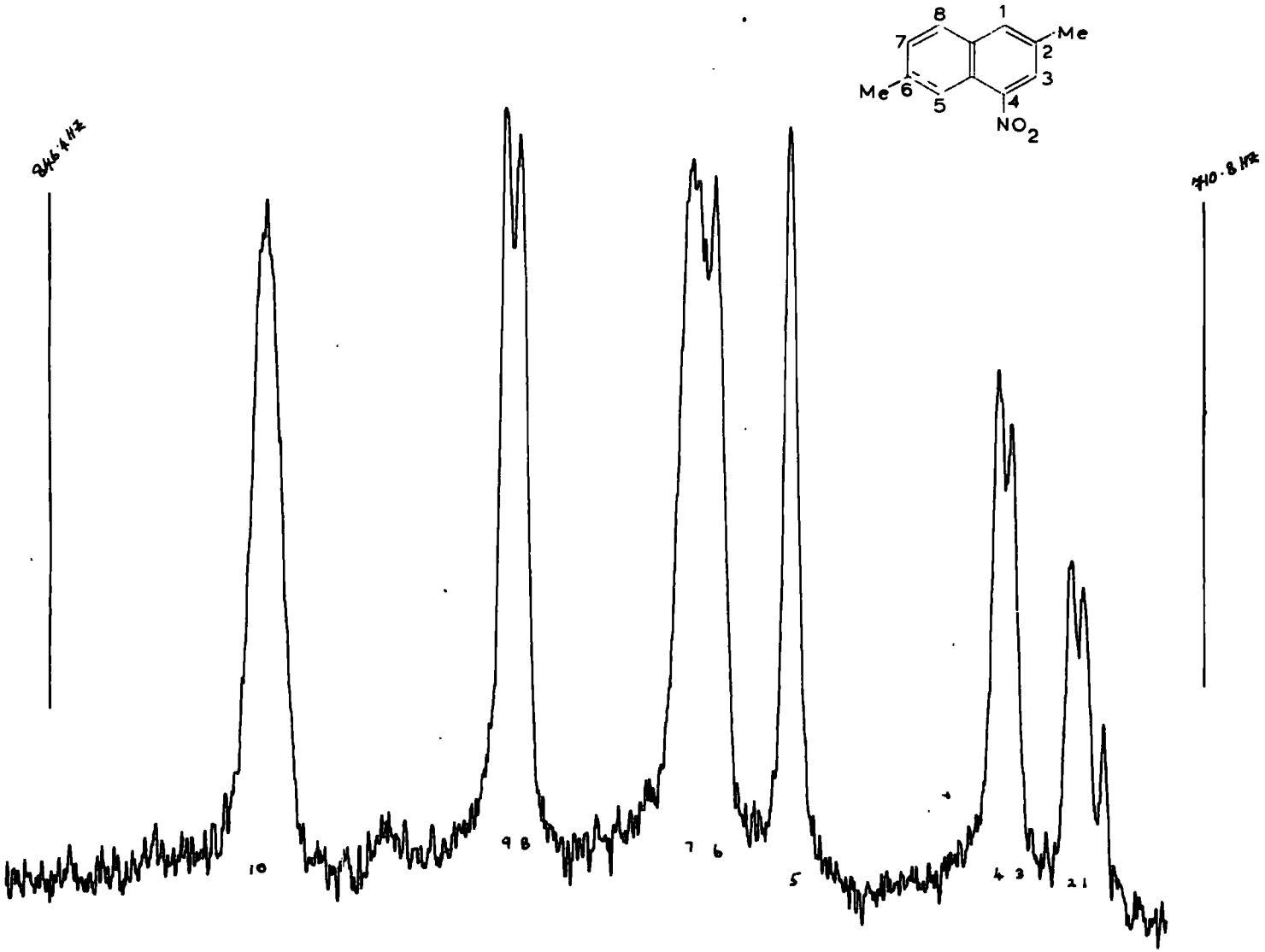
2,6-Dimethyl-4-nitronaphthalene

Spectrum(b) shows the low field aromatic region of 2,6-dimethyl-4-nitronaphthalene(in carbon tetrachloride), with a sweep width of 250Hz. The methyl groups(not shown)

(a)



(b)



form a singlet at τ 7.50. From the data of Wells[173] for the effect of a nitro group on the chemical shift of a methyl group, it is found that the predicted splitting of the methyl peaks in 2,6-dimethyl-4-nitronaphthalene is 0.02ppm, while in the 3-nitro isomer the predicted splitting is 0.2 ppm. Thus the methyl peaks in the 4-nitro isomer would be observed as a singlet. Using the INDOR double resonance technique, the following assignment was made.[172]

Peaks	Proton	Peaks	Proton
1, 2, 3, 4	7	7	1(or 3)
		8, 9	3(or 1)
5, 6	8	10	5

The INDOR experiments show that spectrum(a) contains an AB and an ABC system. The AB coupling constant is 8.1c/s, characteristic of a 1-2 coupling constant.[173] Thus the assignment of spectrum(a) as 1-nitro-2,6-dimethylnaphthalene is unambiguous. (τ_A-τ_B= 0.43 ppm) The INDOR experiments show that spectrum(b) also contains an AB and an ABC system. The AB coupling constant is 1.6c/s, characteristic of a 1-3 coupling constant, so that the assignment of spectrum (b) as 4-nitro-2,6-dimethylnaphthalene is unambiguous. (τ_A-τ_B = 0.22 ppm)

CHAPTER 6

MO Calculations of Ground and Excited State Properties of Methyl-Substituted Benzenes and Naphthalenes.

Models for a Theoretical Treatment of Substituent Effects

Any theory of substituent effects should encompass a theoretical interpretation of as many experimentally observable quantities as possible. Thus it might be possible to explain:

a) Frequency shifts and changes in intensity of electronic transitions of aromatic compounds on substitution.

b) Changes in orbital energies as evidenced by ionisation potentials.

c) Changes in charge distribution as evidenced by changes in ^{13}C and ^{1}H chemical shifts.

d) Relative reactivities of substituted aromatic compounds and positional selectivity within the aromatic ring.

The theoretical considerations will initially be mainly concerned with the effect of methyl substituents. Craig and Doggett[4] have shown that intensity changes in the electronic spectrum of benzene, on methyl-substitution, can be accounted for by assuming that the methyl group has an inductive perturbation only. However, Murrell et al.[3] have shown, from Petruska's analysis of experimental results,[21] within the framework of the localised orbital model, that a methyl group exerts a mesomeric and an inductive effect.

The influence of a methyl group on reactivities has been treated by inductive and mesomeric models.[69,71,75]

Clark and Emsley[5] made calculations on substituted

benzenes, within the framework of the PPP SCF MO method, treating the effect of the substituent as:

i) purely mesomeric

ii) mesomeric + σ-inductive

iii) mesomeric + σ and pi-inductive

The energies and intensities of the lowest singlet-singlet transitions calculated by methods i) and iii) showed similar agreement with experimental results, but only the combined inductive-mesomeric model(iii) gave good agreement with ^{1}H and ^{13}C chemical shifts. The distribution of the pi-electrons in a substituted benzene is usually more sensitive to the method of calculation than the relative energies of excited states. These results showed that good agreement with observed quantities could not be obtained if the inductive effect was neglected.

In this thesis, methyl-substituted benzenes have been investigated using a) a pure mesomeric, and b) an inductive-mesomeric model. In addition, toluene has been studied using a pure inductive model.

Using a), the frequency shifts and intensity changes of the 2600, 2050 and 1850Å bands of benzene, on methyl-substitution, showed agreement with experimental data on a par with the results obtained using b). However, the calculated changes in ionisation potential, on methyl-substitution, using the mesomeric model, were considerably lower than the experimental data. Much better agreement

was obtained using the inductive-mesomeric model.

Using the pure inductive model for toluene, all the above properties were considerably underestimated.

All of these results demonstrate that the best model, for both ground and excited states, is one combining inductive and mesomeric effects.

.....

Results

1) Frequency Shifts and Intensity Changes of Electronic Transitions of Aromatic Compounds on Methyl Substitution.

Table 1 gives the calculated and observed frequency shifts of the benzene singlet-singlet transitions, on methyl substitution. Two models were used for the calculations:

a) pure mesomeric

b) inductive-mesomeric.

In addition, a pure inductive model(c) was used for toluene. The experimental data were taken from ref.21.

It can be seen that a pure inductive model is inadequate, while the mesomeric and inductive-mesomeric models give similar agreement.

In table 2, calculated and observed oscillator strengths(f) are listed. Oscillator strengths tend to be overestimated by MO theory, possibly due to the zero-overlap approximation. In order to give a clearer picture of the effect of substituents, the change in f on methyl-substitution is given, and the ratio $\Delta f_X/\Delta f_{Toluene}$.

Table 1

Frequency Shifts of the 2600Å, 2050Å and 1850Å Bands of Benzene on Methyl Substitution.

Position of Methyl Groups	Model	Frequency Shifts (cm^{-1})					
		2600Å		2050Å		1850Å	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	c	16		8		8	
	a	653		1339		1331	
	b	782	610	1500	1400	1436	1400
1,2	a	1194		2452		2629	
	b	1379	920	2863	1900	2750	2100
1,3	a	1129		2105		2710	
	b	1194	1150	2218	2500	2863	2700
1,4	a	1395		2508		1831	
	b	1904	1390	2549	2900	1920	2500
1,3,5	a	1492		2637		3283	
	b	1347	1520	2597	3300	3452	3300

Table 2

Changes in Oscillator Strengths of the 2600, 2050 and 1850Å Bands on Methyl Substitution.

Position of Methyl Groups	Model	$f_X - f_{Benzene}$ (calc.)			(obs.)	$\Delta f_X / \Delta f_{Toluene}$	
		2600Å $\times 10^{-4}$	2050Å	1850Å	2600Å $\times 10^{-4}$	calc.	obs.
1	c	29	0	-0.001		1	
	a	66	0.059	-0.006		1	
	b	186	0.070	-0.017	10	1	1
1,2	a	87	0.052	+0.029		1.31	1.1
	b	248	0.065	-0.005	11	1.33	
1,3	a	62	0.034	+0.053		0.93	1.2
	b	179	0.031	+0.033	12	0.96	
1,4	a	233	0.156	-0.025		3.52	3.4
	b	611	0.164	-0.031	34	3.28	
1,3,5	a	0	0	+0.026		0	0
	b	0	0	+0.016	0	0	

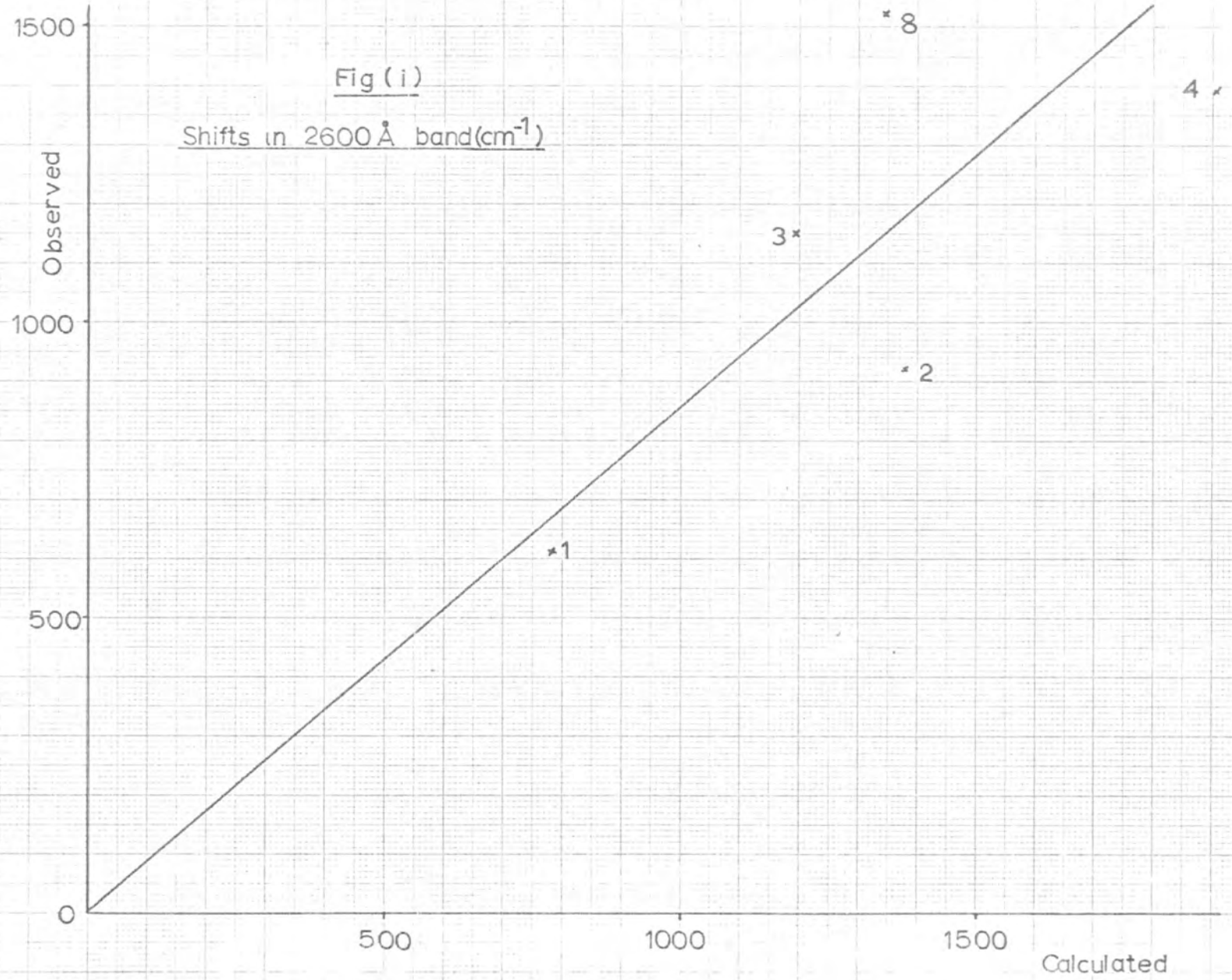
In figures (i)→(iii) observed frequency shifts are plotted against calculated frequency shifts for the benzene 2600, 2050 and 1850Å bands, on methyl-substitution, using an inductive-mesomeric model. (The numbering system is as in Table 8). In each case there is a good linear correlation. Figure(iv) shows observed $\Delta f_X/\Delta f_{Toluene}$ values plotted against the calculated values, using the mesomeric and the inductive-mesomeric models. A similar linear correspondence is obtained in each case.

Table 3 shows the calculated wavelengths and oscillator strengths of the first three singlet-singlet transitions of the benzenium cation, on methyl-substitution, using an inductive-mesomeric model.

From the electronic spectra of benzene, toluene and mesitylene in HF/BF_3 solutions,[168] the wavelengths of the first band for the benzenium, toluene-4 and mesitylene cations are obtained as 4200, 4070 and 3850Å, respectively. Thus the observed wavelength shifts of the toluene-4 and mesitylene cations relative to the benzenium cation are respectively -130 and -350Å, in contrast to the calculated values of -175 and +247Å, respectively. The shift of the toluene cation is successfully predicted while the calculated shift for the mesitylene cation is at variance with the observed value. From the results of Dallinga et al.[169] the wavelengths of the first two absorption bands of

Fig (i)

Shifts in 2600 Å band (cm^{-1})



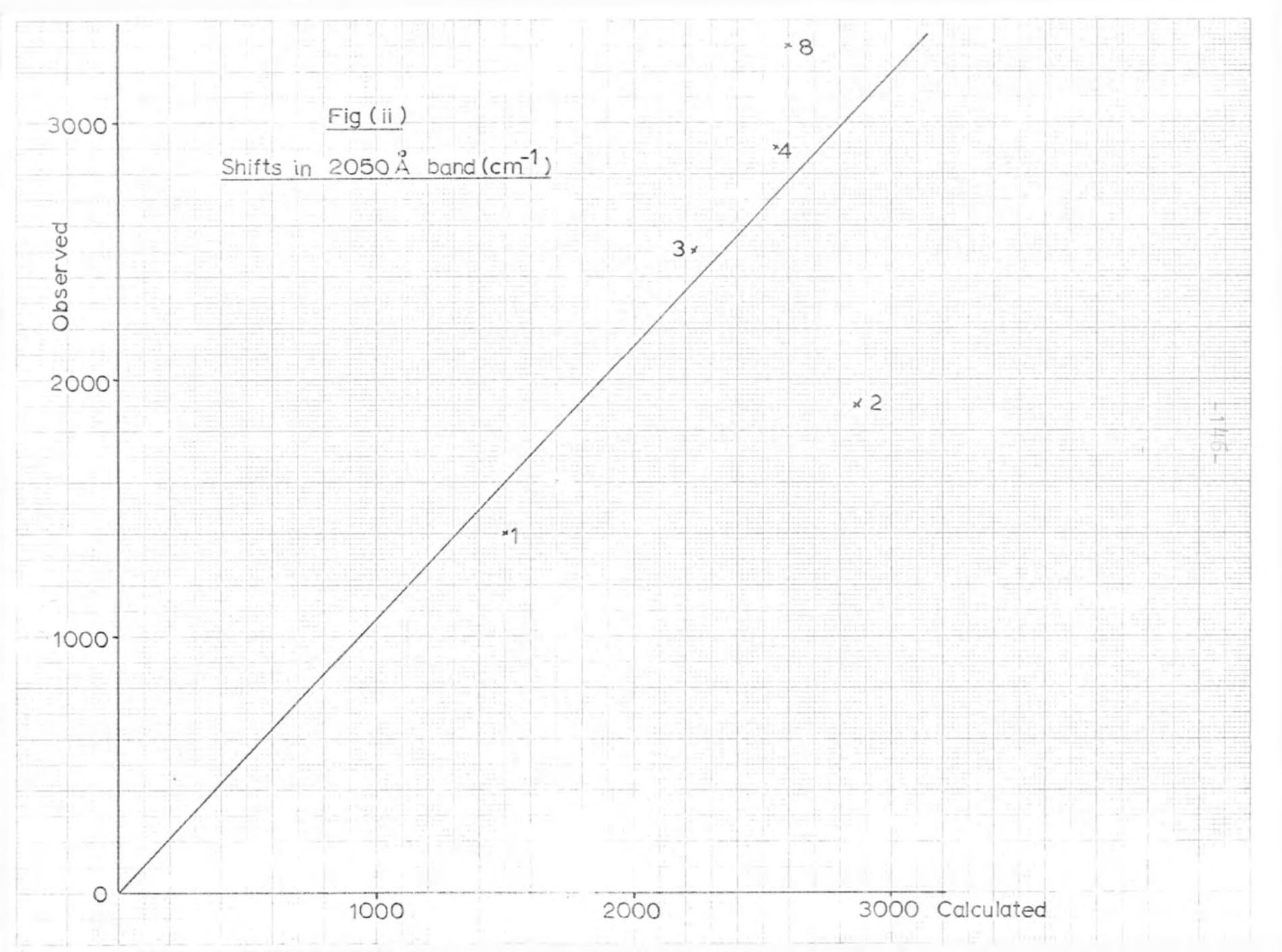
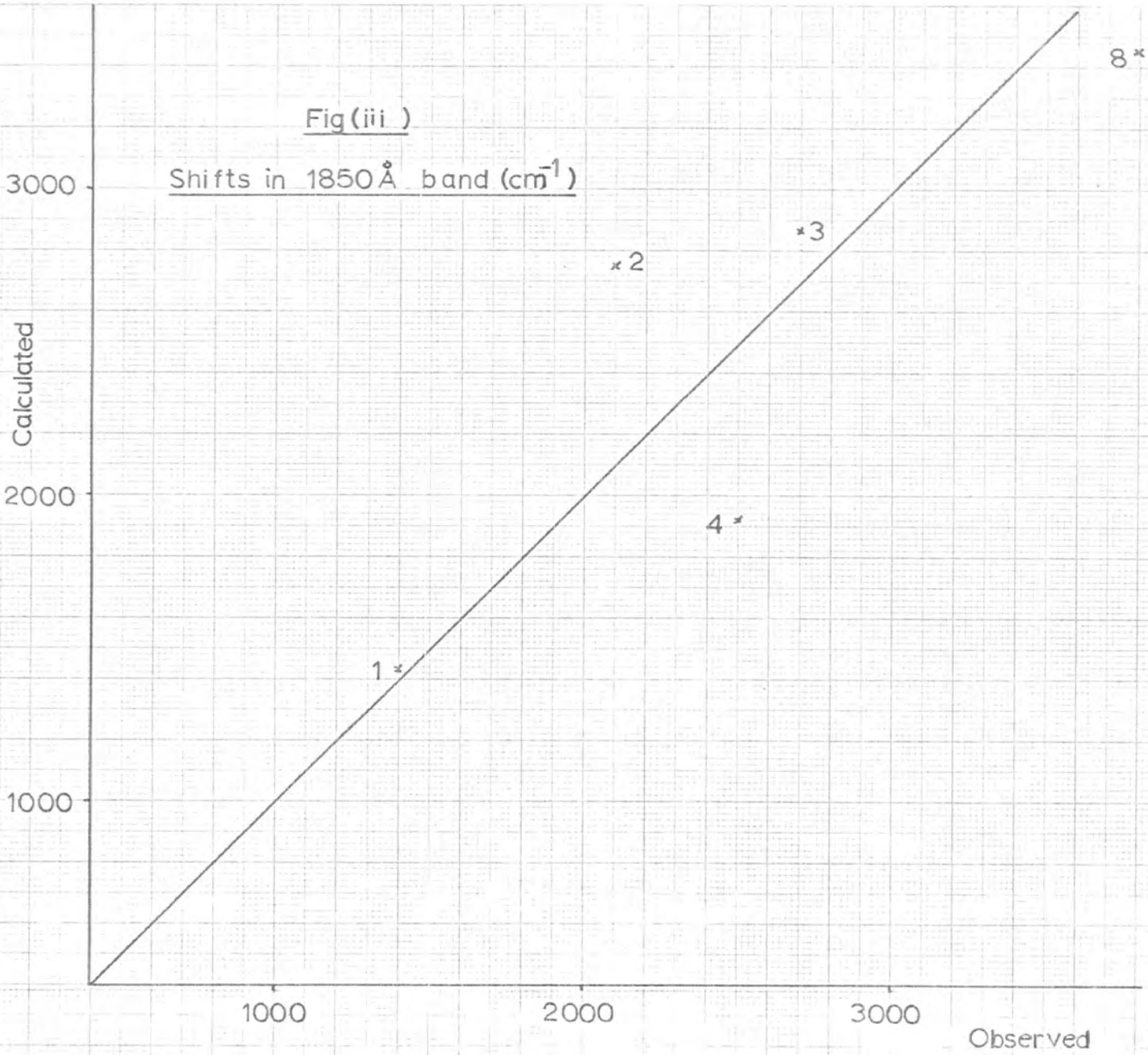


Fig (ii)
Shifts in 2050 Å band (cm^{-1})
Observed
Calculated
0
1000
2000
3000
×1
×2
3×
×4
×8

Fig (iii)

Shifts in 1850 Å band (cm^{-1})



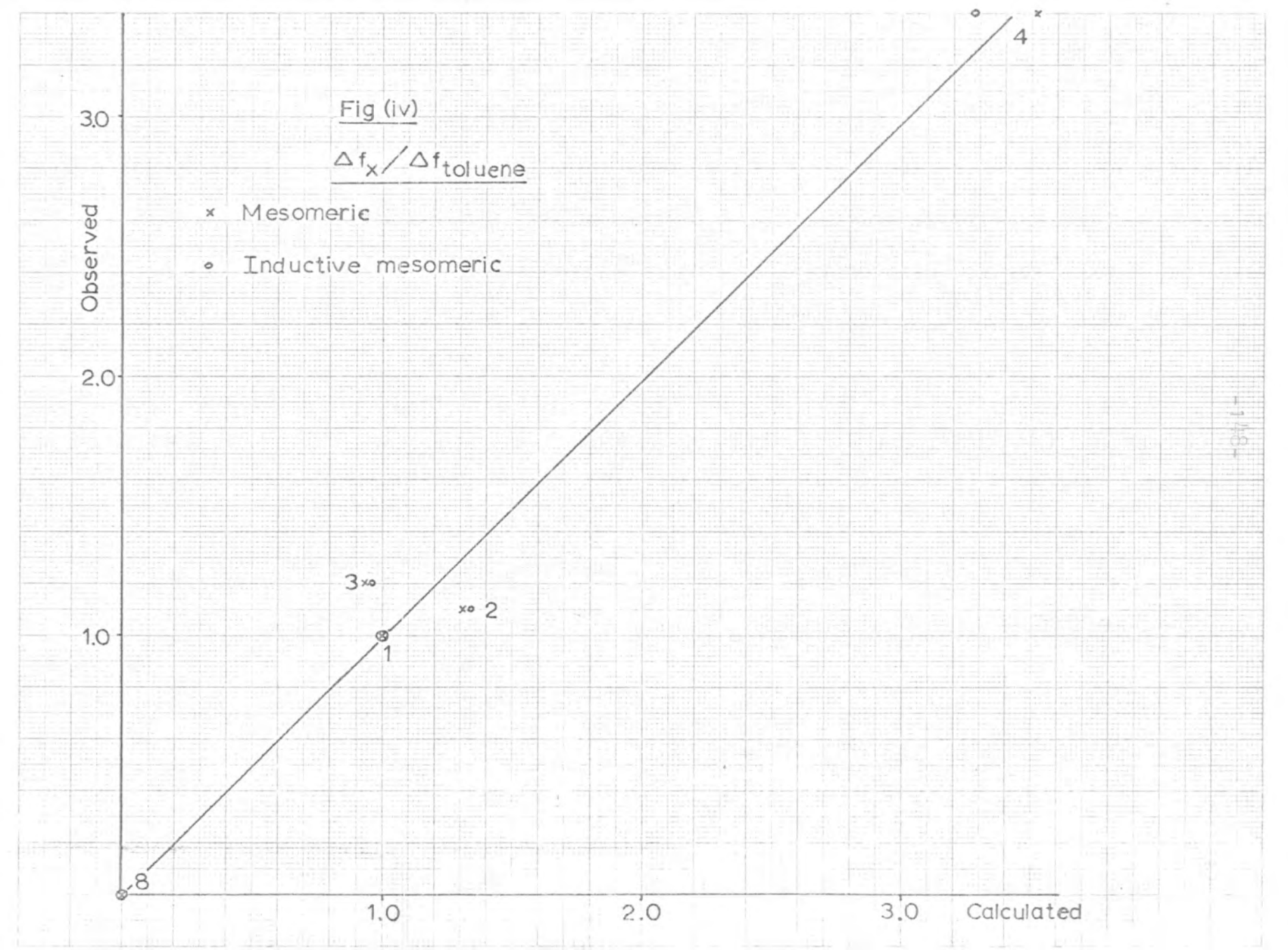


Fig (iv)
$\Delta f_x / \Delta f_{toluene}$
× Mesomeric
○ Inductive mesomeric
Observed
Calculated
3.0
2.0
1.0
1.0
2.0
3.0
4
3
2
1
8

Position of Methyl Groups	Singlet - Singlet Transitions		
...	3534 (0.3034)	2313 (0.1138)	1746 (1.080)
1	3756 (0.3812)	2336 (0.1527)	1971 (0.4258)
2	3995 (0.2553)	2756 (0.1237)	2205 (0.0505)
3	3359 (0.2464)	2657 (0.3875)	1879 (0.3982)
1,2	4121 (0.3723)	2638 (0.0503)	2193 (0.0760)
1,3	3581 (0.3440)	2633 (0.3645)	1960 (0.5829)
1,4	4137 (0.3099)	2734 (0.2220)	2167 (0.1039)
1,5	4004 (0.4241)	2355 (0.1837)	1657 (0.6641)
2,3	3809 (0.2190)	2824 (0.2889)	2231 (0.0605)
2,4	4212 (0.2662)	3208 (0.0855)	2340 (0.0867)
1,3,5	3781 (0.3648)	2655 (0.4267)	2030 (0.6901)

Table 3

The spectra calculated for a number of methyl-substituted benzenium ions; wavelengths in Å; oscillator strengths between brackets.

mesitylene in HF/BF_3 are 3550 and 2560Å. These absolute values show reasonable agreement with the calculated values, but using their quoted values for the benzenium cation of 3700 and 2600Å for the first two bands, a hypsochromic shift is again observed as opposed to the calculated bathochromic shift.

There is a considerable difference between the wavelengths obtained from Reid's paper[168] and those obtained from that of Dallinga et al.[169] There is no other data available at present, so that it is not possible to reach any real conclusions as to the validity of these calculated spectra.

2. Changes in Charge Distributions as Evidenced by Changes in ^{13}C and ^{1}H Chemical Shifts.

There is a close correspondence between ^{13}C and ^{1}H resonances observed at the para position of monosubstituted benzenes, where the primary contribution to the relative shifts arises from the inductive and mesomeric effects of the substituent. In the para position therefore, where magnetic anisotropy effects are at a minimum, a correlation is expected between the pi-electron density and chemical shifts.[171] Such a correlation cannot be expected in polysubstituted benzenes, because all positions will be affected by magnetic anisotropy and other interfering effects which do not depend on the pi-electron distribution. However, the results of Clark and Emsley[5] show that in

monosubstituted benzenes, good agreement can be obtained between ^{13}C and ^{1}H chemical shifts at the para positions (relative to the shift in benzene) and the corresponding electron density change, calculated using an inductive-mesomeric model.

The charge density distributions for methyl-substituted benzenes and naphthalenes, and their cations, are given in Tables 5, 6 and 7.

3. Changes in Ionisation Potential of Aromatic Compounds on Methyl-Substitution.

Table 4 shows the calculated and observed ionisation potentials of a series of aromatic compounds, with the change in ionisation potential calculated relative to benzene. The observed ionisation potentials are taken from ref. 170.

It can be seen that a pure inductive or mesomeric model considerably over-estimates the ionisation potential, while the inductive-mesomeric model brings the calculated values much nearer to the experimental data. Again, the theoretical models give overestimated values, so that a better comparison can be made using changes in ionisation potential relative to benzene. The correlation between theory and experiment is very good, considering the approximations involved, although the ionisation potential of mesitylene is considerably overestimated.

Table 4

Changes in Ionisation Potential of Aromatic Compounds on Methyl Substitution

Compound	Model	Ionisation Potentials		$I_y - I_{Benzene}$	
		calc.(eV)	obs.(eV)	calc.	obs.
Benzene		9.783	9.245	0	0
Toluene	c	9.648		0.135	
	a	9.554		0.229	
	b	9.404	8.82	0.379	0.425
o-Xylene	a	9.414		0.369	
	b	9.167	8.555	0.616	0.690
m-Xylene	a	9.430		0.353	
	b	9.209	8.56	0.574	0.685
p-Xylene	a	9.345		0.438	
	b	9.063	8.445	0.720	0.800
mesitylene	a	9.320		0.463	
	b	9.141	8.27	0.642	0.975
naphthalene	b	8.914	8.12	0.869	1.125
1-Methyl-naphthalene	b	8.700	7.96	1.083	1.285
2-Methyl-naphthalene	b	8.775	7.95	1.008	1.295
2,6dimethyl naphthalene	b	8.619		1.164	

Table 5

Ground State pi-Electron Density Distributions.

(Inductive-Mesomeric Model)

C_8	C_9	C_{10}	Me	Me	Me
			1.9688		
			1.9712	1.9712	
			1.9689	1.9689	
			1.9704	1.9704	
			1.9690	1.9690	1.9690
1.0000	1.0000	1.0000			
1.0021	1.0284	0.9948	1.9672		
1.0057	0.9934	1.0132	1.9686		
0.9994	1.0065	1.0065	1.9692	1.9692	

Table 6

The Ground-State pi-Electron Density Distributions of Methyl-Substituted Benzene Cations

Compound	C_1	C_2	C_3	C_4	C_5	C_6	Me	Me	Me
Benzene cation		0.7006	0.9642	0.6703	0.9642	0.7006			
Toluene-2-cation	0.6539		0.7569	0.9712	0.7000	1.0155	1.9026		
Toluene-3-cation	0.9021	0.7602		0.7107	0.9621	0.7105	1.9543		
Toluene-4-cation	0.6405	0.9994	0.7271		0.7271	0.9994	1.9064		
o-Xylene-3-cation	0.9474	0.7013		0.7701	0.9682	0.7461	1.9589	1.9079	
o-Xylene-4-cation	0.6723	0.9367	0.7917		0.7320	0.9979	1.9113	1.9580	
m-Xylene-2-cation	0.7011		0.7011	1.0259	0.7187	1.0259	1.9136	1.9136	
m-Xylene-4-cation	0.6651	1.0555	0.6788		0.7729	1.0015	1.9148	1.9114	
m-Xylene-5-cation	0.8999	0.7517	0.8999	0.7696		0.7696	1.9548	1.9548	
p-Xylene-2-cation	0.6604		0.8121	0.9244	0.7293	1.0135	1.9043	1.9559	
Mesitylene cation	0.7184		0.7184	1.0609	0.6807	1.0609	1.9200	1.9208	1.9200

Table 7

The Ground-State pi-Electron Density Distributions of Methyl-Substituted Naphthalene Cations.

(Inductive-Mesomeric Model)

C_6	C_7	C_8	C_9	C_{10}	Me	Me
0.9538	0.8484	0.9624	0.9214	1.0338		
0.8236	0.9505	0.8920	1.0065	0.8627		
0.8439	0.9550	0.9703	1.0519	0.8806	1.9026	
0.9499	0.8312	0.9777	0.8830	1.0060	1.9589	
0.8648	0.9557	0.9088	1.0623	0.9304	1.9151	
0.7346	0.9880	0.7066	1.0573	0.9314	1.9437	
	0.8634	0.9838	0.9067	1.0028	1.9571	
0.8688		0.6753	1.0220	0.8812	1.9405	
0.9836	0.7257		0.9736	1.0285	1.9593	
0.9554	0.8691	0.9670	0.9457	1.0427	1.9108	
0.9533	0.8360	0.9865	0.8594	1.0038	1.9297	
0.8523	0.9546	0.8955	1.0307	0.9226	1.9587	
0.7226	0.9839	0.6893	1.0279	0.9358	1.9578	
	0.8603	0.9879	0.8651	1.0129	1.9361	
0.8539		0.6667	1.0014	0.8719	1.9560	
0.9857	0.7423		0.9147	1.0422	1.9407	
0.8889	0.9111	0.9641	0.9618	1.0371	1.9118	1.9587
0.8870	0.8704	0.9827	0.8670	0.9990	1.9306	1.9568
0.7876	0.9948	0.8919	1.0393	0.9157	1.9595	1.9415

4. A Comparison between Calculated Changes in Localisation Energies and Relative Reactivities of Substituted Aromatic Hydrocarbons.

The above results show that for ground or excited state properties, the best agreement between observed and calculated results is obtained using an inductive-mesomeric model. This was therefore used to calculate cation localisation energies. In chapter 3, eq.5, it was shown that the logarithm of the relative reaction rate is proportional to the difference of the pi-energy changes between the reactants and the transition states. With the assumption that the transition state can be represented as a Wheland intermediate, this difference in pi-energy changes is proportional to the difference of the cation localisation energies. In Table 8, the cation localisation energies($\Delta E_{\pi b}$), and the difference of the cation localisation energies of various hydrocarbons and of benzene($\Delta E^{X}_{\pi b} - \Delta E^{o}_{\pi b}$), are given.

Using the partial rate factors for these hydrocarbons, measured as described in chapter 5, graphs were drawn of the logarithms of the partial rate factors versus $\Delta\Delta E_{\pi b}$. (Figures 1→7; the hydrocarbons and cations are labelled as in Table 8.)

Figure 1 shows the plot for methyl-substituted benzenes. There is a very reasonable correlation, with the m-xylene-2-position showing the greatest deviation. This

Table 8

Localisation Energies of the Cations of Methyl-Substituted Benzene and Naphthalene Compounds.

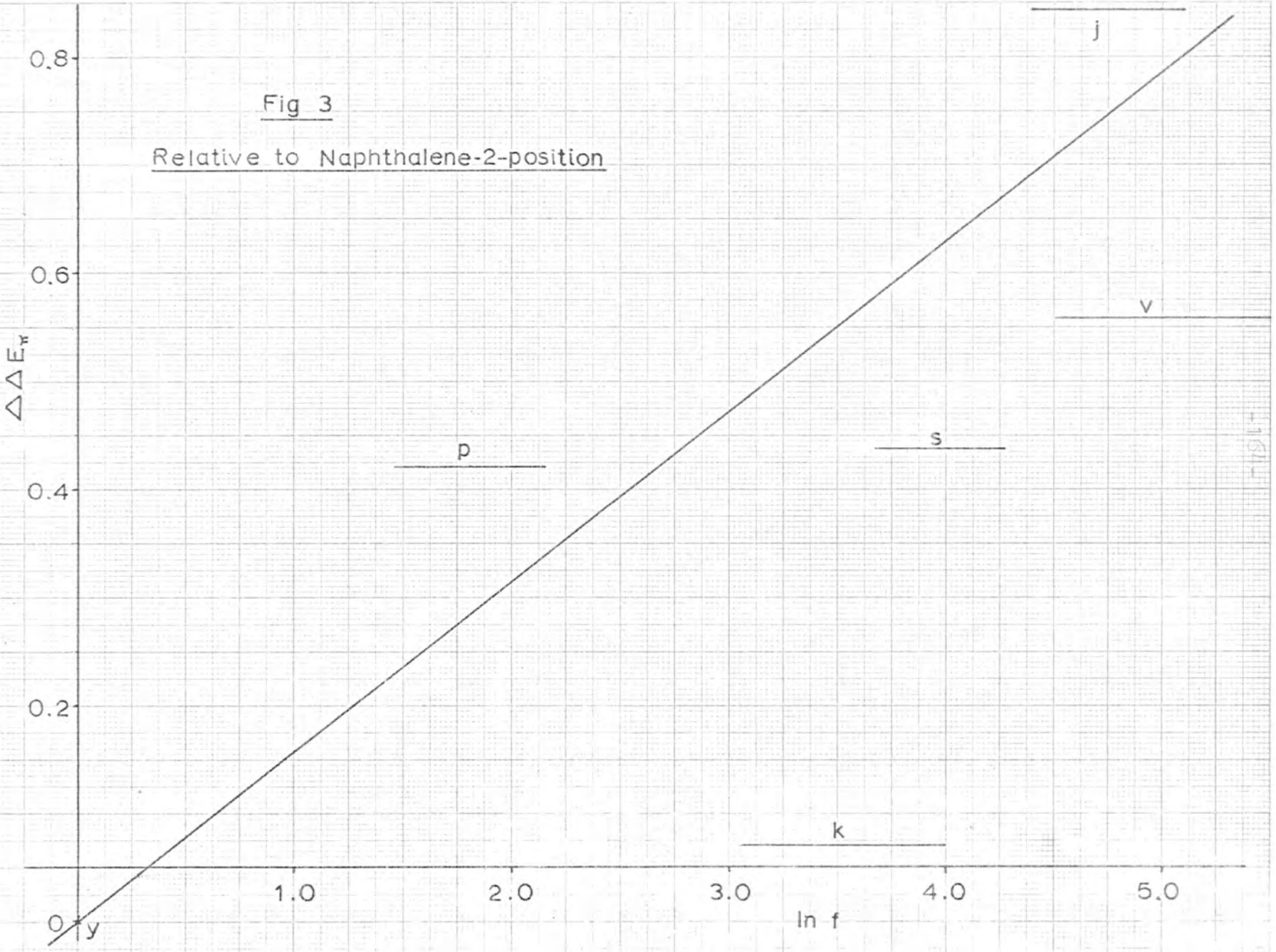
(Inductive-Mesomeric Model)

Compound	pi-Bonding energy(eV)	Cation	pi-Bonding energy(eV)	$\Delta E_{\pi b}$	$\Delta E^{X}_{\pi b} - \Delta E^{O}_{\pi b}$
2-Methyl naphthalene(7)	-156.823	1(o)	-135.777	21.047	-1.465
		3(p)	-135.150	21.673	-0.839
		4(q)	-135.141	21.682	-0.830
		5(r)	-135.190	21.633	-0.879
		6(s)	-135.167	21.656	-0.856
		7	-134.864	21.960	-0.552
		8(t)	-135.445	21.378	-1.134
2,6-Dimethyl naphthalene(9)	-192.887	1(u)	-171.969	20.918	-1.594
		3(v)	-171.351	21.536	-0.976
		4(w)	-171.588	21.299	-1.213

is expected to show deviation because of steric hindrance. If the methylbenzenes and methylnaphthalenes are plotted on one graph with partial rate factors and $\Delta\Delta E_{\pi b}$ values relative to benzene, there is no linear correlation for the results as a whole. It appears more reasonable to consider the reactivities of substituted naphthalenes relative to naphthalene. Figures 2 and 3 show the graphs for substitution at α and β positions respectively. In each case there is a considerable spread of results, but there is some linear correlation. Figures 4→7 show the plots for positions adjacent and non-adjacent to methyl groups on separate graphs. In each case the deviations from linearity are considerable, but the errors in the partial rate factors are of a similar order. Thus it is reasonable to conclude from these results that SCF MO theory can be successfully applied to the calculation of reactivities of substituted hydrocarbons.

Fig 3

Relative to Naphthalene-2-position



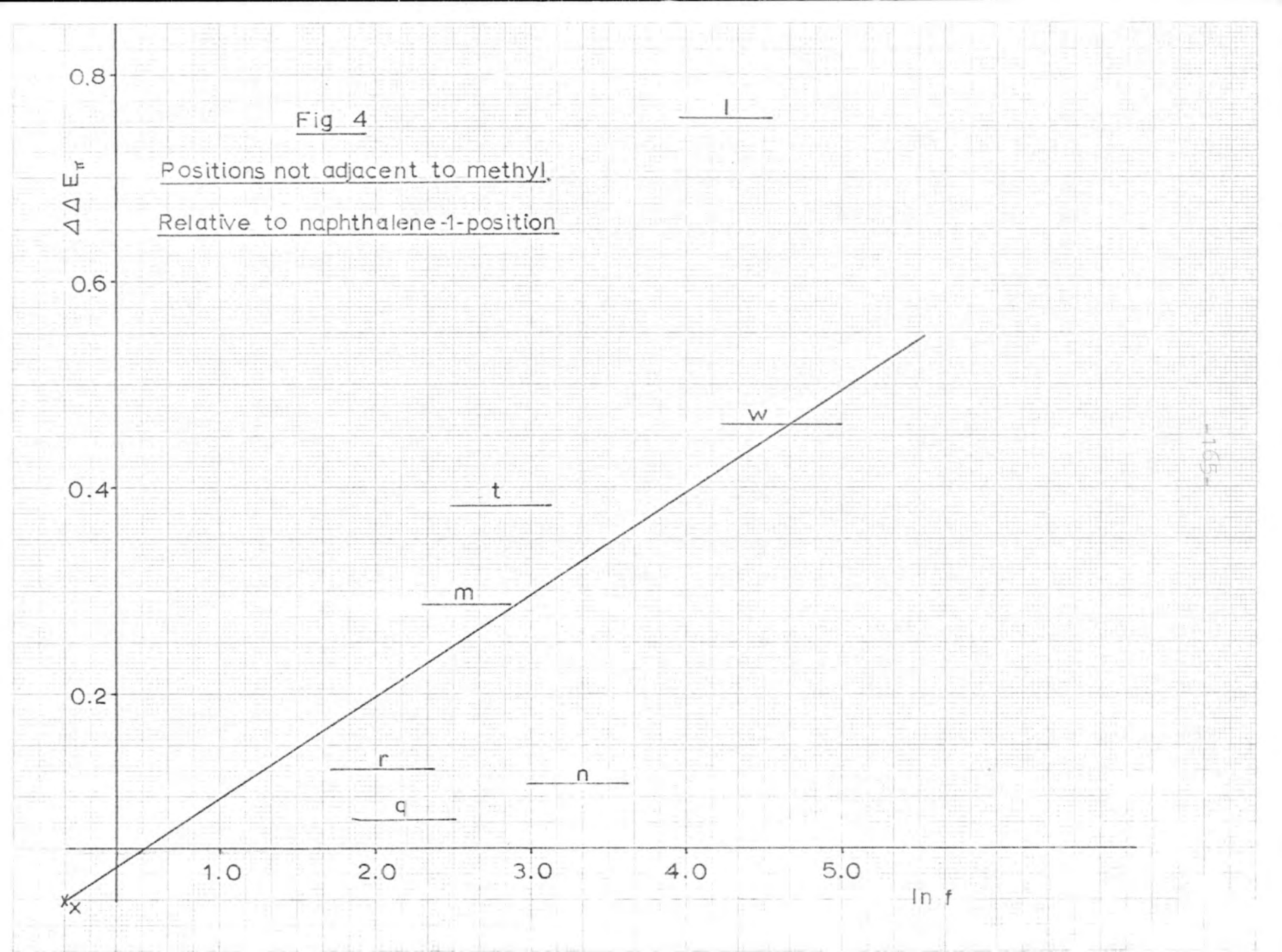


Fig 4
Positions not adjacent to methyl.
Relative to naphthalene-1-position
$\Delta\Delta E_{\pi}$
0.8
0.6
0.4
0.2
l
w
t
m
r
n
q
1.0
2.0
3.0
4.0
5.0
ln f

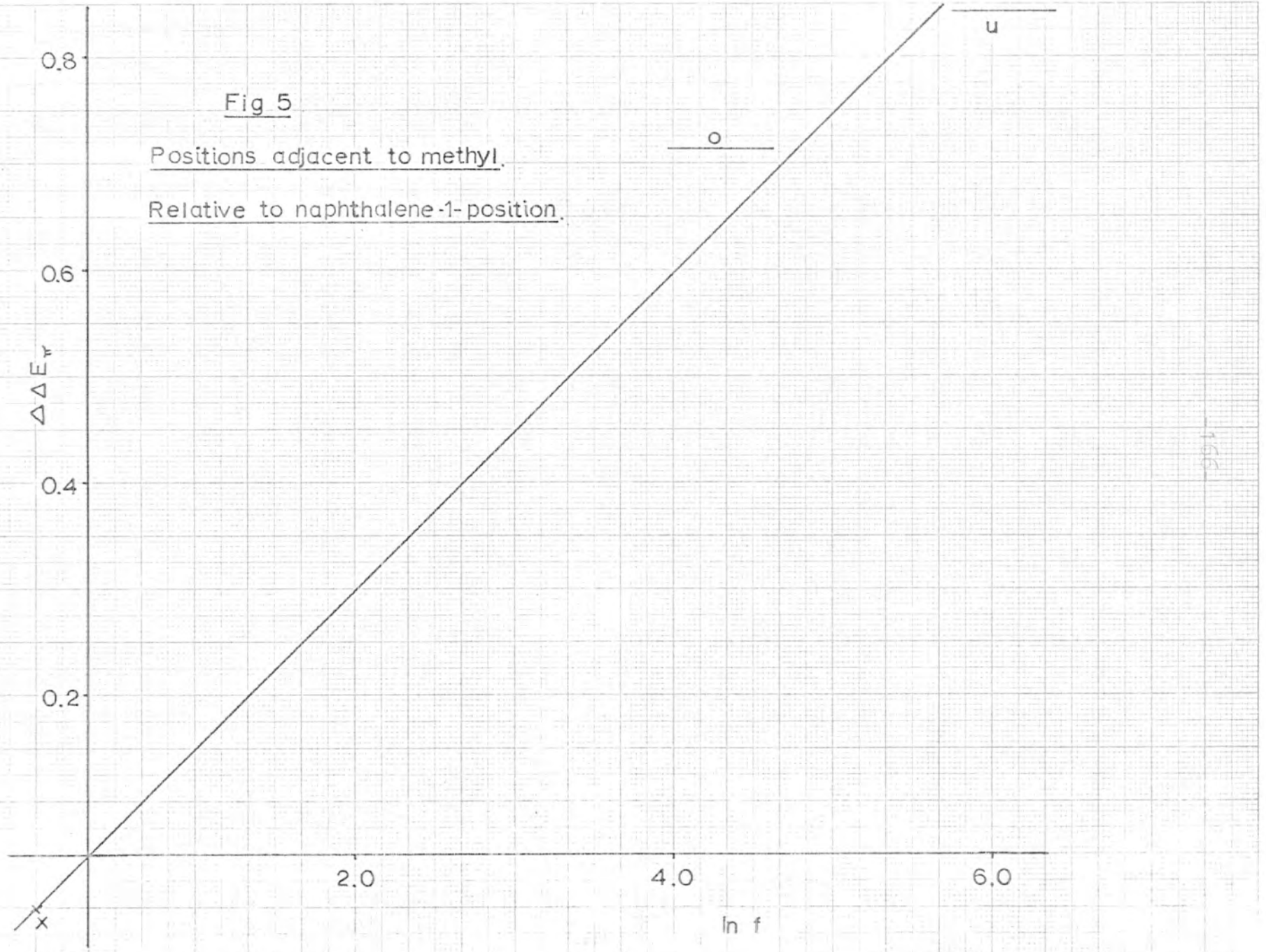
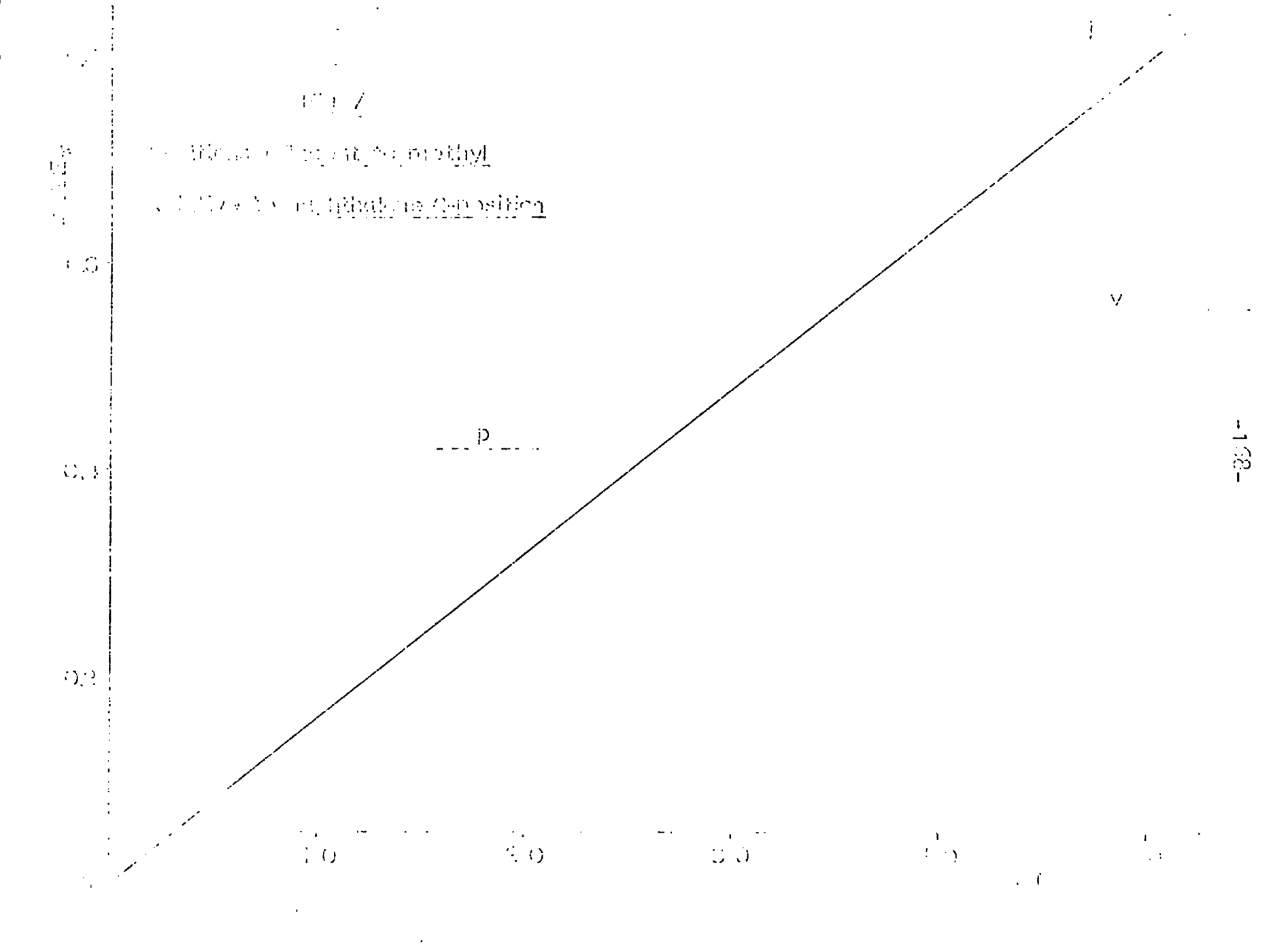


Fig 5
Positions adjacent to methyl.
Relative to naphthalene-1-position.
u
o
0.8
0.6
0.4
0.2
ΔΔE_r
2.0
4.0
6.0
ln f

Fig 6

Positions not adjacent to methyl.

Relative to naphthalene 2 position.

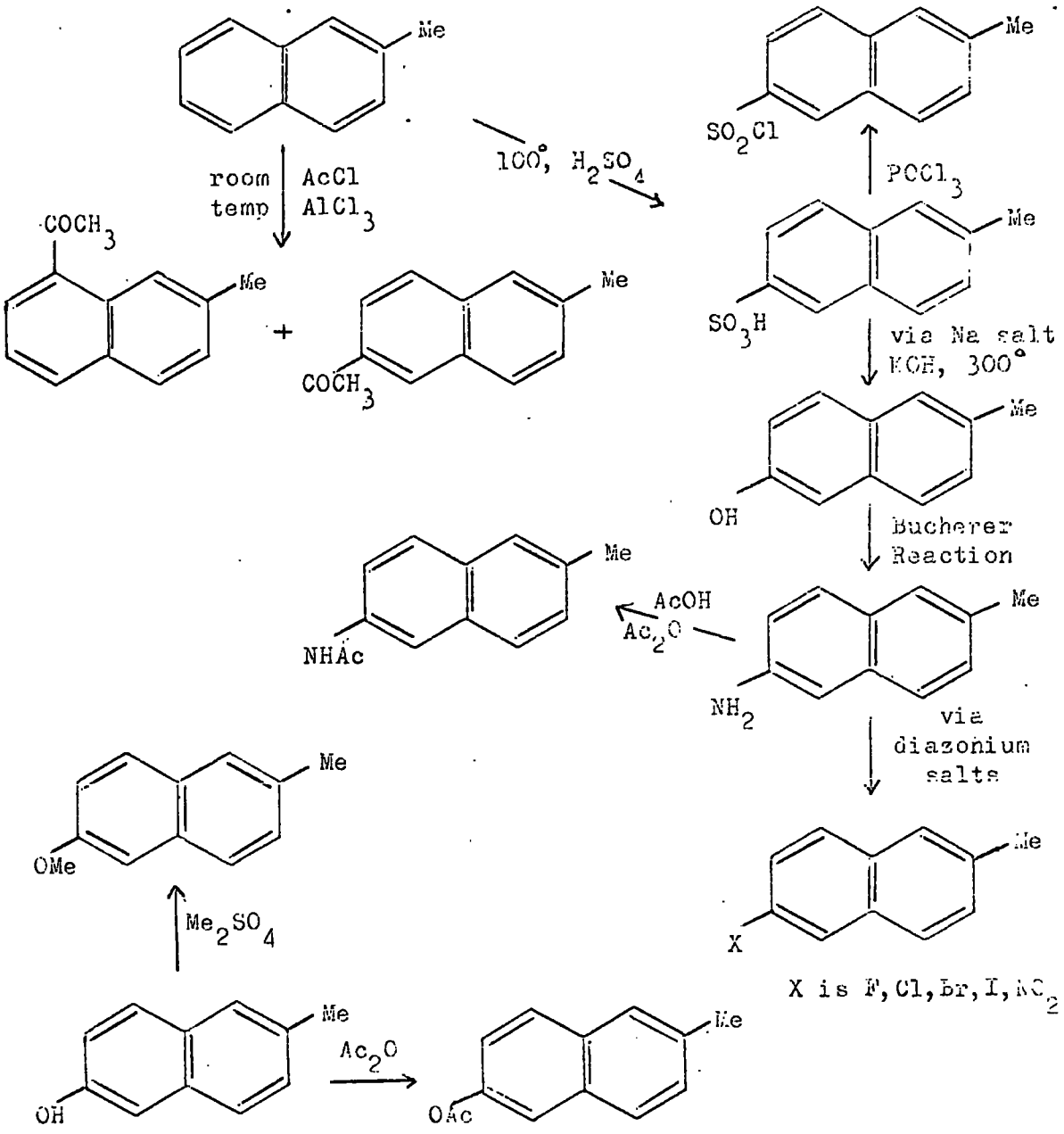


CHAPTER 7

The Preparation of 6-Substituted 2-Methylnaphthalenes.

Discussion of Experimental Work

The following reaction scheme was used to prepare a series of 6-substituted 2-methylnaphthalenes:

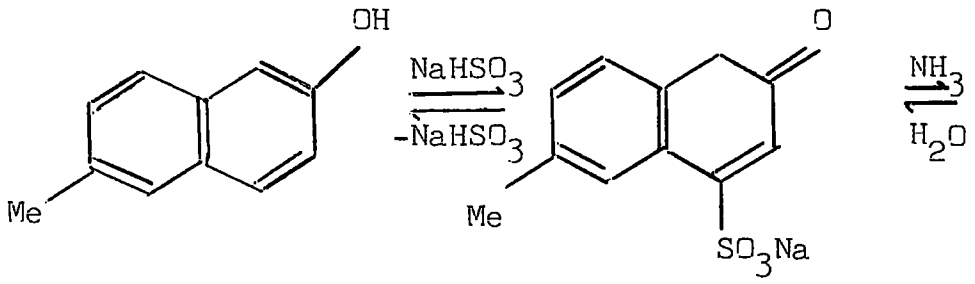


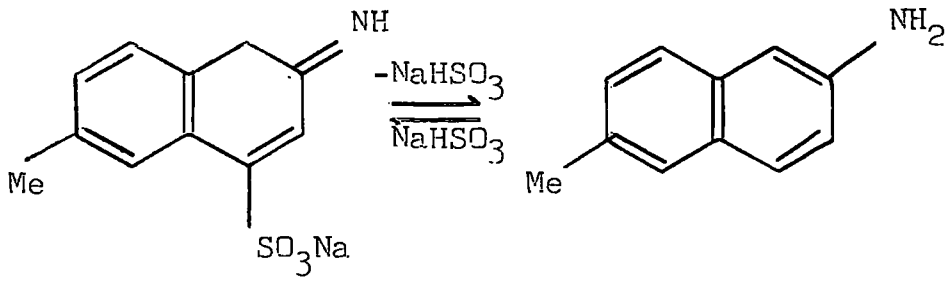
2-Methylnaphthalene was converted, in more than 90% yield, to 2-methylnaphthalene-6-sodium sulphonate by the method of Dziewonski et al.,[157] though yields were improved by reducing the reaction time from 6 to 3 hr. At 95-100°, the 6-isomer is formed almost quantitatively, but at 40° the 8-sulphonic acid and at 160° the 7-sulphonic acid are the major products.[158]

2-Methylnaphthalene-6-sodium sulphonate was converted in high yield to 2-hydroxy-6-methylnaphthalene, by fusion with KOH at 280-300°.[157] This was converted in near quantitative yields to 2-methoxy and 2-acetoxy 6-methylnaphthalenes, by shaking alkaline solutions with dimethyl sulphate and acetic anhydride, respectively.[157]

The Bucherer reaction was used to convert 2-hydroxy-6-methylnaphthalene in 80% yield to 2-amino-6-methylnaphthalene. The method used was essentially that of Dziewonski et al., but a Carius tube was used in preference to an autoclave.

In 1967, Seeboth[159] proposed that the Bucherer reaction proceeds via the intermediate formation of tetralone and tetralonimine sulphonic acids according to the following simplified scheme:





A similar mechanism will apply, using ammonium sulphite and aqueous ammonia.

2-Amino-6-methylnaphthalene was converted to 2-acetamido-6-methylnaphthalene by shaking with a mixture of glacial acetic acid and acetic anhydride.[157]

When a diazonium salt solution is run into a solution of a cuprous halide dissolved in the corresponding halogen acid, the diazonium group is replaced by a halogen atom. This, the Sandmeyer reaction, was used to prepare 2-chloro and 2-bromo 6-methylnaphthalenes. The mechanism of the Sandmeyer reaction has been investigated by Hodgson et al.[160] and by Cowdrey and Davies,[161] who suggested a slow coordination between ArN_2^+ and $CuCl_2^-$ to form the complex $ArN_2.CuCl_2$ from which an aryl radical is generated:

$$Ar\text{-}N\quad N\ldots Cl\text{-}Cu\text{-}Cl \xrightarrow[\text{slow}]{} Ar^{\cdot} + N_2 + CuCl_2$$

followed by displacement of a chlorine atom from $CuCl_2$:

$$Ar^{\cdot} + Cl\text{-}Cu\text{-}Cl \xrightarrow[\text{fast}]{} Ar\text{-}Cl + CuCl$$

2-Iodo-6-methylnaphthalene was prepared by a nucleophilic displacement of N_2 by I^-.

2-Fluoro-6-methylnaphthalene was obtained in high

yield[162] by a Balz-Schiemann reaction involving decomposition of the diazonium tetrafluoroborate by gentle heating in an inert atmosphere. There is little experimental evidence to shed light on the mechanism of the decomposition, though Hodgson et al.[160] suggested an intramolecular displacement reaction.

The preparation of 2-methyl-6-nitronaphthalene was rather unsuccessful. The decompositions of the diazonium cobaltinitrite and tetrafluoroborate were attempted according to the methods of Hodgson and Marsden,[163] and Starkey,[164] respectively, but the highest yield obtained was ca. 5%.

Diazonium nitrites decompose in nitrous acid solution to form nitro-compounds, the mechanism appearing to be attack of the carbon atom, to which the diazonium group is attached, by anionoid nitrogen of the nitrous acid molecule. The mechanism of the decomposition of diazonium cobaltinitrites and tetrafluoroborates would be expected to be similar,[163] with nucleophilic attack by the nitrite ion.

2-Methylnaphthalene-6-sulphonyl chloride was prepared by the method of Marrian and Evans,[165] by heating 2-methylnaphthalene-6-sodium sulphonate with phosphorus oxychloride at 100°.

$$2ArSO_2ONa + POCl_3 \rightarrow 2ArSO_2Cl + NaPO_3 + NaCl$$

2-Methylnaphthalene was acylated by the method of Kon and Weller[166] to give 1-acetyl-7-methylnaphthalene and 2-

acetyl-6-methylnaphthalene in about equal amounts. The isomers were separated via their semi-carbazones, the derivative of 2-acetyl-6-methylnaphthalene being much less soluble in aqueous ethanol than that of 1-acetyl-7-methylnaphthalene.

Experimental

2-Methylnaphthalene-6-Sulphonic Acid

Sulphuric acid (45 ml, S.G. 1.84) was added dropwise to molten 2-methylnaphthalene, (60 g) stirring at 100°. The mixture was stirred at 100° for 3 hr. and then poured into cold water (200 ml). Potassium carbonate (20 g) was added, and the solution saturated at its boiling point with sodium chloride. On cooling the solution, the 6-sulphonic acid crystallised as its sodium salt, leaving the unwanted isomers in solution. One crystallisation of the crude sodium salt (89 g, 86%) from sodium chloride solution (10% w/v) gave 2-methylnaphthalene-6-sodium sulphonate as white flakes, m.p. > 360°.

2-Hydroxy-6-Methylnaphthalene

2-Methylnaphthalene-6-sodium sulphonate, (82 g) prepared as above and dried at 130°, was mixed to a paste with water (16 g) and added in portions to molten potassium hydroxide, (200 g) stirring at 280°. The temperature of the melt was raised to 280-300° for 15 min. After cooling, the reaction mixture was dissolved in water (400 ml) and the

crude 2-hydroxy-6-methylnaphthalene precipitated with concentrated hydrochloric acid. After filtration, the residue was steam-distilled, filtered, washed with water, and dried to give fairly pure 2-hydroxy-6-methylnaphthalene. (42 g, 80%) Recrystallisation from petroleum ether (b.p. 80-100°) gave colourless prisms, m.p. 128-129°. (lit.[157] 128-129°)

2-Methoxy-6-Methylnaphthalene

2-Hydroxy-6-methylnaphthalene (4.3 g) was dissolved in a minimum of sodium hydroxide solution (10% w/v) and diluted with water (10 ml). Dimethyl sulphate (3.5 ml) was run into the solution, and the flask shaken for 10 min. The white precipitate was filtered, washed with water and dried. A further amount of dimethyl sulphate (2 ml) was added to the filtrate, which was again shaken for 10 min. The precipitate was filtered, washed and dried, and combined with the first batch. Sublimation (0.01 mm, 25°) afforded a white solid, m.p. 71-73° (4.6 g, 98%). Crystallisation from petroleum ether (b.p. 60-80°) gave 2-methoxy-6-methylnaphthalene as colourless flakes, m.p. 77-78°. (lit.[157] 78-79°)

2-Amino-6-Methylnaphthalene

Sulphur dioxide was passed through ammonia solution (10 ml, d.0.880), cooled in ice, until the gain in weight was 2.5 g. The ammonium sulphite solution was sealed in a 100 ml Carius tube with 2-hydroxy-6-methylnaphthalene (10 g),

aqueous ammonia solution (10 ml, d.0.880), and water(30ml). After shaking at 150° for 12 hr., the tube was opened and the contents extracted with ether. The light-brown solid obtained after removal of the ether was extracted with dilute hydrochloric acid(2N, 500 ml) for 24 hr. in a Soxhlet apparatus. The amine was liberated by pouring the hot solution, after filtration, into excess cold sodium hydroxide solution(50% w/v). After cooling, the solution was filtered and the pale pink solid dried under vacuum. Sublimation (70°, 0.001 mm) afforded a white solid, m.p. 127-129°.(7.8 g, 78%) Crystallisation from aqueous ethanol gave 2-amino-6-methylnaphthalene as white needles, m.p. 129-130°.(lit.[157] 129-130°).

6-Methylnaphthalene-2-Diazonium Tetrafluoroborate

A thin paste of 2-amino-6-methylnaphthalene(7.8 g, 0.05 mole) in a mixture of concentrated hydrochloric acid (8 ml) and water(20 ml) was cooled to 5° and diazotised with a solution of sodium nitrite(3.5 g, 0.05 mole) in water(5 ml). After a half hour at 0-5°, a solution of sodium tetrafluoroborate(7.6 g, 0.07 mole) in water(20 ml) was gradually stirred into the diazonium mixture. This was stirred at 0-5° for a further 2 hr., before filtering off the yellow precipitate and washing with water(10 ml), methanol(10 ml) and ether.(3 portions of 20 ml) The diazonium tetrafluoroborate(10.6 g, 82%) was dried in vacuum over concentrated sulphuric acid for 24 hr.

2-Fluoro-6-Methylnaphthalene

The dry 6-methylnaphthalene-2-tetrafluoroborate(10.6 g) was decomposed under nitrogen, by careful application of a small luminous flame to the outside of the flask. After decomposition, the 2-fluoro-6-methylnaphthalene(6 g, 95%) was sublimed(0.001 mm, 25°) direct from the flask. Crystallisation from petroleum ether(b.p. 60-80°) gave white flakes, m.p. 77°.(lit.[162] 77°)

2-Chloro-6-Methylnaphthalene

A slurry of 2-amino-6-methylnaphthalene(3.9 g, 25 mmole) in a solution of concentrated hydrochloric acid (5 ml) and water(10 ml) was diazotised at 0° with a solution of sodium nitrite(1.8 g, 25 mmole) in water(3 ml).

Copper sulphate(16 g) and sodium chloride(6 g) were dissolved in boiling water(50 ml), and a solution of sodium bisulphite(5 g) in water(20 ml) added with shaking, during 5 min. The solution was cooled to room temperature and filtered at the pump. After washing with a few ml. of distilled water, the white cuprous chloride was dissolved in concentrated hydrochloric acid(20 ml).

The diazonium mixture was poured slowly, with constant shaking, into the cuprous chloride solution, maintaining the temperature at 60°. After 1 hr., the mixture was heated for 10 min. at 100° to ensure complete decomposition of the deep-brown complex. The solution was cooled, filtered, and the dried residue extracted with ether. Evap-

oration of the ether afforded impure 2-chloro-6-methylnaphthalene(2.0 g, 46%) which was purified by column chromatography using activated alumina as stationary phase and benzene as eluent. Two recrystallisations from petroleum ether(b.p. 60-80°) gave white flakes, m.p. 122-123°. (Found: C, 74.6;H, 5.0; $C_{11}H_9Cl$ requires C, 74.8;H, 5.1%).

2-Bromo-6-Methylnaphthalene

Copper sulphate(19.2 g), copper turnings(6 g), sodium bromide(46.2 g), concentrated sulphuric acid(6 ml, S.G. 1.84) and water(300 ml) were refluxed for 4 hr. A little sodium bisulphite was added to ensure complete reduction.

Hydrobromic acid(70 g, 48%) was added to a slurry of 2-amino-6-methylnaphthalene(6.3 g, 40 mmole) in water(100 ml). The mixture was cooled to 5° and well-stirred while a solution of sodium nitrite(4.5 g, 76 mmole) in water(7.5 ml) was added over a period of 3-4 hr. The resulting diazonium mixture was poured during 10 min. into the cuprous bromide solution(prepared as above) at 70-80°. After leaving overnight at room temperature, the mixture was steam-distilled to give 2-bromo-6-methylnaphthalene(3.0 g, 35%). Crystallisation from petroleum ether(b.p. 60-80°) gave white flakes, m.p. 142°. (lit.[162] 142°)

2-Iodo-6-Methylnaphthalene

2-Amino-6-methylnaphthalene(1.9 g) was diazotised as described above(Prep. of 2-chloro-6-methylnaphthalene).

Potassium iodide(2.2 g) in water(2.2 g) was added to the well-stirred diazonium mixture, over 30 min. The solution was allowed to warm up to room temp. and left stirring for 3-4 hr. After this time, the solution was heated for 10 min. at 100°, cooled, extracted with ether(3 times), and dried($MgSO_4$). Evaporation of the ether afforded impure 2-iodo-6-methylnaphthalene, (1.5 g, 46%) which was purified by eluting with n-hexane down a 30x2 cm. alumina column. (Camag 100-240 mesh, alkaline, Brockmann activity 1). Crystallisation from n-hexane gave white flakes, m.p. 143-144°. (lit.[165] 146-147°)

2-Acetamido-6-Methylnaphthalene

A mixture of glacial acetic acid(1.5 ml) and acetic anhydride(1.5 ml) was added to 2-amino-6-methylnaphthalene (2.5 g) and the mixture shaken for 10 min. After pouring into cold water(100 ml), 2-acetamido-6-methylnaphthalene (3.1 g, 92%) was filtered off and dried under vacuum(0.001 mm). Crystallisation from petroleum ether(b.p. 75-95°) and again from benzene gave pale pink needles, m.p. 154-155°. (lit.[157] 155-156°)

2-Acetoxy-6-Methylnaphthalene

Acetic anhydride(7 ml) was added to a mixture of 2-hydroxy-6-methylnaphthalene(9.1 g), sodium hydroxide solution(100 ml, 10% w/v) and crushed ice(100 g). The mixture was shaken for 15 min., filtered, and the residue washed with cold sodium hydroxide solution(50 ml, 10% w/v) and

water. The dried residue(10.6 g, 88%) was shown by glc (10% NGA/90-100 mesh celite, 150°) to be about 90% pure 2-acetoxy-6-methylnaphthalene. Recrystallisation(twice) from n-hexane gave white flakes, m.p. 108-109°.(Found: C, 77.7;H, 5.6; $C_{13}H_{12}O_2$ requires C,78.0;H, 6.0%).

Attempted Preparation of 2-Methyl-6-Nitronaphthalene

a) From the Diazonium Tetrafluoroborate

6-Methylnaphthalene-2-diazonium tetrafluoroborate (1.9 g) was added as a thin aqueous paste, in small portions, to a well-stirred suspension of copper bronze (1 g) in a solution of sodium nitrite(4 g) in water(8 ml) at room temp. The reaction mixture was left stirring at room temp. until evolution of nitrogen ceased, extracted with ether, dried($MgSO_4$), and the ether removed. Purification by column chromatography yielded but 30 mg.(2.5%) of 2-methyl -6-nitronaphthalene. Crystallisation from petroleum ether (b.p. 75-95°) gave yellow needles, m.p. 118-120°.(lit.[167] 119-120°).

b) From the Diazonium Cobaltinitrite

A thin paste of 2-amino-6-methylnaphthalene(1.57 g, 10 mmole) in a solution of conc. hydrochloric acid(2 ml) and water(6 ml) was cooled to 5° and diazotised with a solution of sodium nitrite(0.7 g, 10 mmole) in water(1 ml). The diazonium mixture was neutralised with calcium carbonate and filtered. Finely powdered sodium cobaltinitrite

(1.5 g) was stirred into the filtrate, and the crystalline diazonium cobaltinitrite filtered off. After drying under vacuum, 2.2 g, (97%) of the diazonium salt were obtained.

The diazonium salt(1 g) was added in portions, at room temp., to a well-stirred solution of sodium nitrite (1 g) in water(6 ml) in which cuprous oxide(0.4 g) was suspended. The mixture was stirred at room temp. for 2 days before being extracted with chloroform. Evaporation of the latter yielded 50 mg. (5.4%) of 2-methyl-6-nitronaphthalene. The m.p. after recrystallisation from petroleum ether(b.p. 75-95°) was 118-120°.

2-Methylnaphthalene-6-Sulphonyl Chloride

2-Methylnaphthalene-6-sodium sulphonate(30 g) was heated for 80 min. at 100 with phosphorus oxychloride(60 g). The reaction mixture was poured on to ice and stirred for 45 min. The solid was filtered off, washed with water, and ground with glacial acetic acid(12 ml). After filtration, it was washed with methanol and dried under vacuum(0.01 mm) to give 2-methylnaphthalene-6-sulphonyl chloride(26 g, 88%). Crystallisation from n-hexane gave white needles, m.p. 92-93°.(lit.[165] 90-92°)

2-Acetyl-6-Methylnaphthalene

2-Methylnaphthalene(46 g) was added to a cold solution of dry aluminium chloride(88 g) in dry nitrobenzene (200 ml). The mixture was cooled in ice and stirred while acetyl chloride(23 g) was carefully added. After stirring

at room temp. for 24 hr., ice and dilute hydrochloric acid were added, the mixture extracted with ether, washed with alkali, and dried($MgSO_4$). After removal of the ether the nitrobenzene was distilled off under reduced pressure. (63° at 1mm) The products from the reaction came over between 140-145°. Gas liquid chromatography(5% NGA, 200°) showed two major fractions in about equal amounts, and at least two minor fractions. The whole distillate was treated with a solution of semi-carbazide hydrochloride(25 g) and sodium acetate(22 g) in water(150 ml). The suspension was warmed, and enough ethanol added to render a homogeneous solution. After heating for 5-10 min., the mixture was cooled and filtered. The residue(31 g) was extracted twice with hot alcohol(250 ml) to give the semi-carbazone of 2-acetyl-6-methylnaphthalene, m.p. 225-227°.(lit.[166] 237°) Without further purification, the semi-carbazone was refluxed for 2 hr. with dilute hydrochloric acid(300ml,2N), and the liberated ketone extracted with chloroform. Evaporation of the chloroform gave 2-acetyl-6-methylnaphthalene (16 g, 30%). Recrystallisation from petroleum ether(b.p. 40-60°) gave white needles, m.p. 65-66°.(lit.[166] 66.5°).

CHAPTER 8

The Nitration of 6-Substituted 2-Methylnaphthalenes.

1. Introduction

In contrast to the amount of work published describing the nitration of substituted benzenes, there have been few quantitative investigations of the nitration of substituted naphthalenes. The most important work published in this field has been the determination of the partial rate factors for the nitration of methyl and methoxy naphthalenes by Alcorn and Wells.[138] There have been several reports of a qualitative nature over the last forty years, and the results for 2- and 2,6- substituted naphthalenes are summarised in Table 1.

Substituent	Nitrating agent	Temp(°C)	Positions of substitution	Reference
2-phenyl	$HNO_3/AcOH$	25	1	175
2-acetamido	ditto	0	1>>8>6	176,177
2-methyl	ditto	25	1>>8>4 5>6>>3	138
2-methoxy	ditto	25	1>>8 6	138
2-nitro	HNO_3/H_2SO_4	-5	8>5	178
2-bromo	HNO_3	25-35	8>>1	179
2,6-dinitro	HNO_3/H_2SO_4	20	8	181
2,6-dimethoxy	$HNO_3/AcOH$	25	1	180
2-acetamido-6-nitro	HNO_3	0	1	182

Table 1 The nitration of 2- and 2,6-substituted naphthalenes

An attempt has been made to provide a quantitative extension of these results, by studying competitive nitrations of a series of 6-substituted 2-methylnaphthalenes and measuring partial rate factors relative to naphthalene. The experimental procedure used was identical to that described in chapter 5, the following compounds being studied: 2-methoxy, 2-fluoro and 2-acetamido-6-methylnaphthalene.

2. Results

Competitive nitrations between naphthalene and 2-fluoro and 2-acetamido-6-methylnaphthalene have been carried out at 25°C in order to measure partial rate factors. For 2-methoxy-6-methylnaphthalene, competitive nitrations were carried out with 2,6-dimethylnaphthalene. From the results of the competitive nitration of the latter(ch.5), partial rate factors relative to naphthalene have been calculated for the former.

Table 2 shows the partial rate factors and isomer distributions that were obtained. Of these results, those for 2-methoxy-5-nitro and 2-fluoro-1-nitro 6-methylnaphthalene are uncertain, as these isomers were not isolated and hence were not identified. The other isomers were characterised by n.m.r. spectroscopy at 100 Mc/s as follows:

Table 2

Partial Rate Factors and Isomer Distributions of 6-Substituted 2-Methylnaphthalenes.

6-Substituent	Isomer Distributions (%)			Partial Rate Factors		
	1-nitro	8-nitro	5-nitro	1-nitro	8-nitro	5-nitro
methoxy* (a)	87.1±0.2	9.6±0.1	3.24±0.15	699±34	348±22	26.2±2.5
methoxy (a)				305000±10400	348000±12900	11400±4000
fluorine (b)	8.3±0.5	25.8±0.8	65.9±1.1	3.42±0.09	10.7±0.6	27.3±1.4
acetamido(a)	100			876±28		

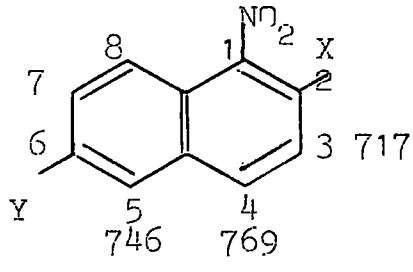
* relative to 2,6-dimethylnaphthalene

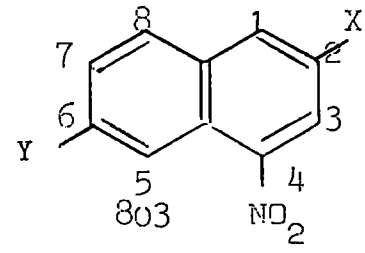
(a) nitric/acetic acid

(b) 30% sulphuric/nitric acid in acetic acid

a) 2-Methoxy-6-Methylnaphthalene

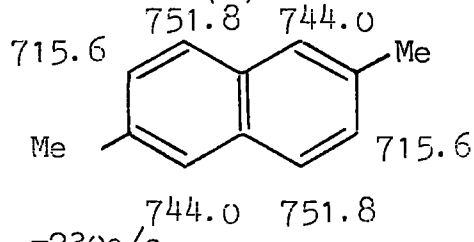
The two isomers isolated from the nitration of 2-methoxy-6-methylnaphthalene were characterised by comparison of their 100Mc/s n.m.r. spectra with those of 1- and 4-nitro-2,6-dimethylnaphthalene, 2,6-dimethylnaphthalene and 2-methoxy-6-methylnaphthalene. Figures (i)-(vi) show the chemical shifts obtained from these spectra(in c/s from TMS at 100Mc/s).

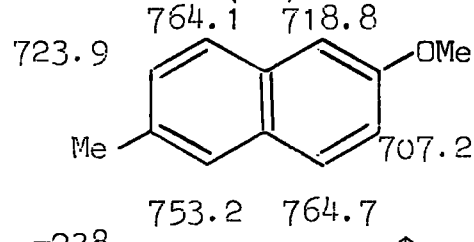




τ_{Me}=246, τ_{OMe}=392, J_{34}=9.3c/s τ_{Me}=258, τ_{OMe}=395, J_{13}=2c/s

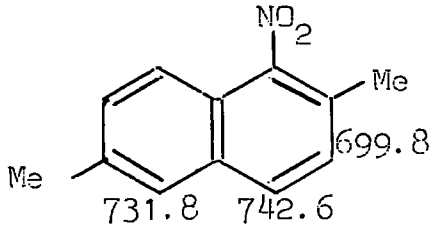
(i) (ii)

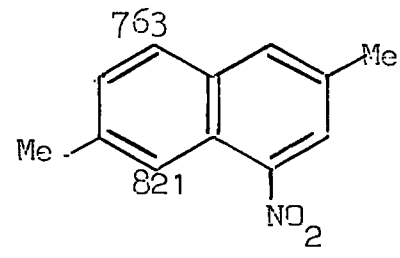




τ_{Me}=230c/s. τ_{Me}=238, τ_{OMe}=370

(iii) (iv)



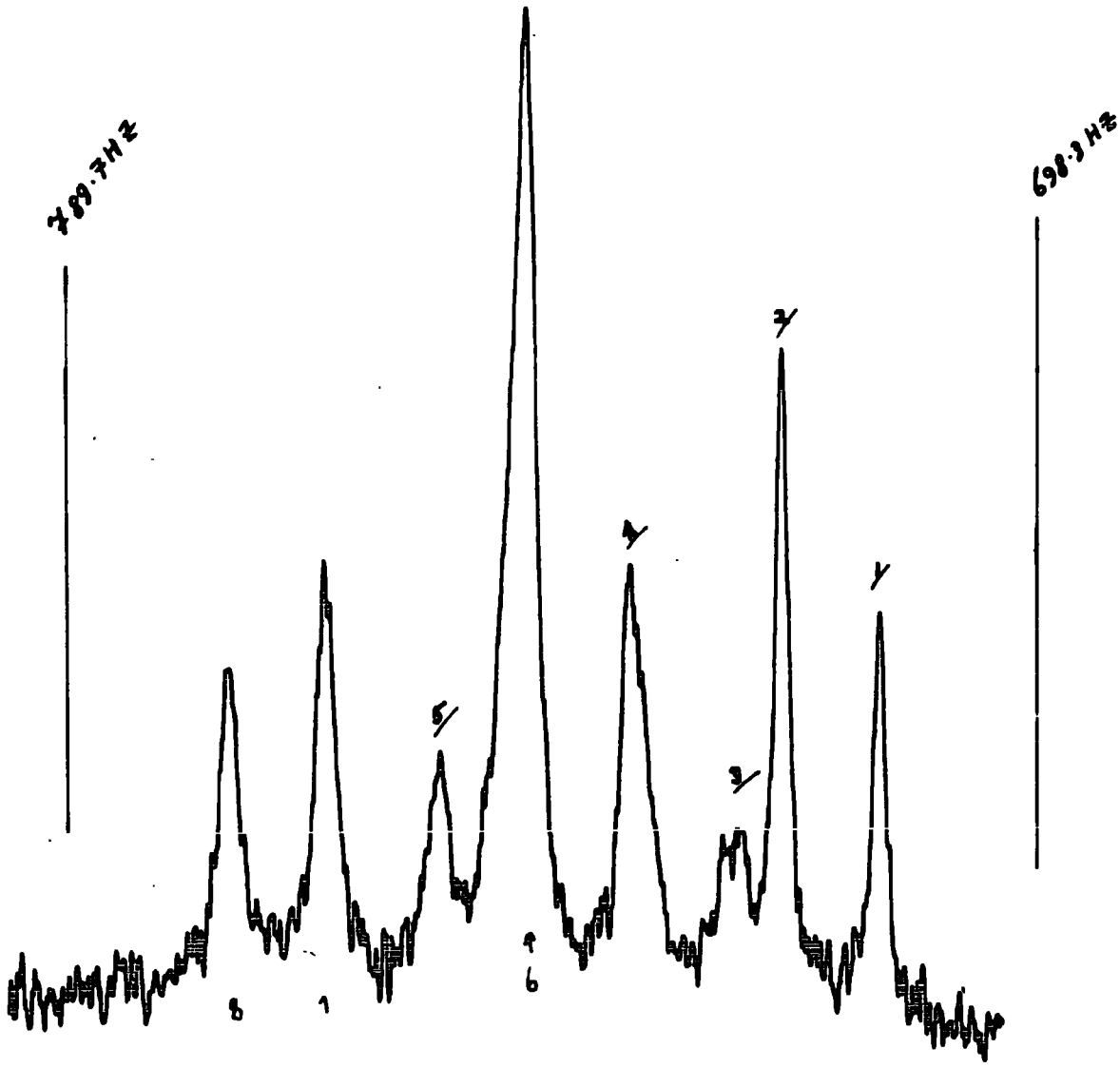


τ_{Me}=228,232 (v) τ_{Me}=250 (vi)

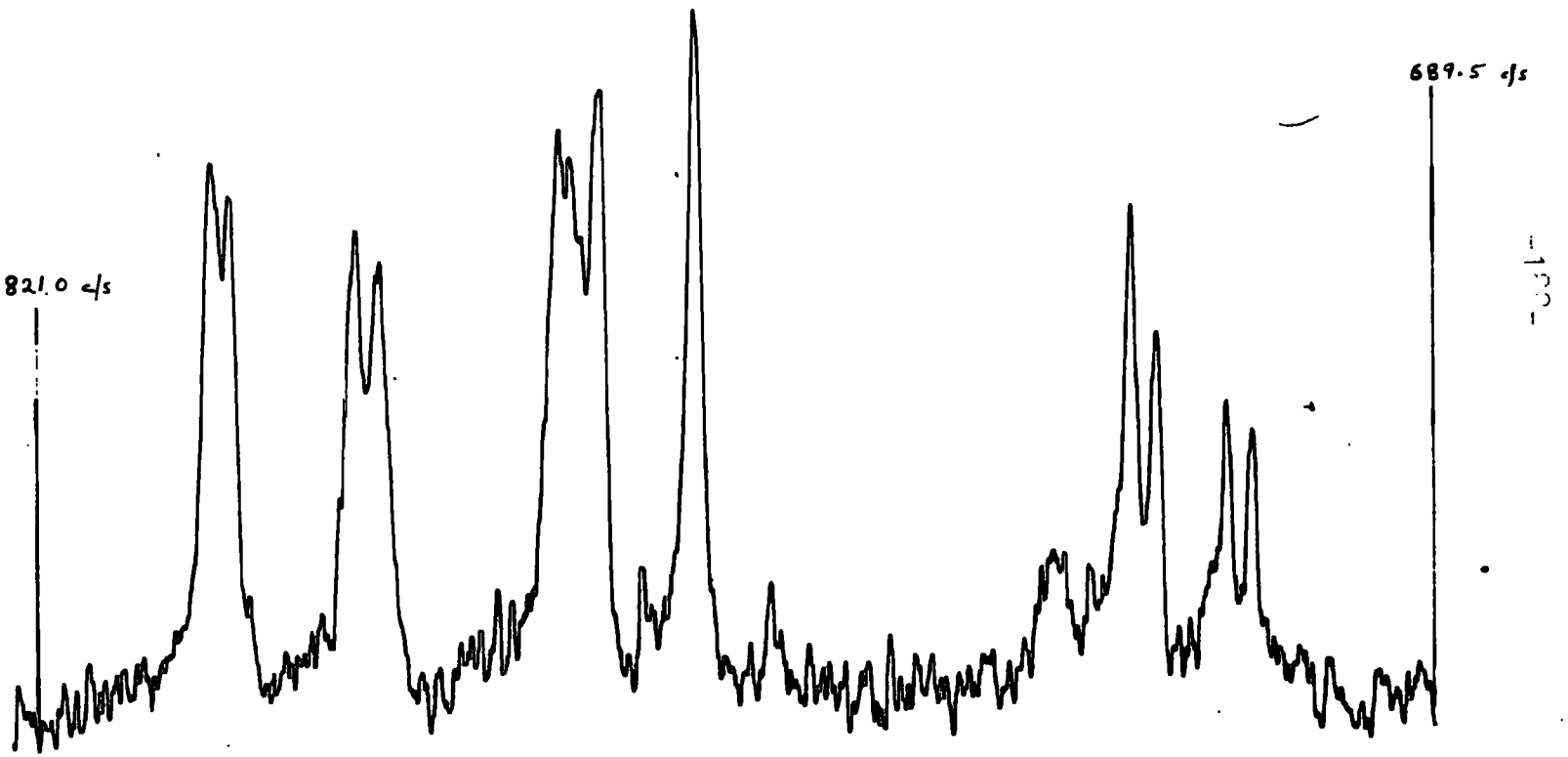
In spectrum(1) it is possible to pick out an AB quartet(peaks 1,2,7 and 8), with coupling constant 9.3 c/s, characteristic of a 1-2 coupling constant. Hence the isomer is of type (i). It is possible to estimate the chemical shift of proton 5(peak 6) as 2.54ppm, compared with 2.47ppm in 2-methoxy-6-methylnaphthalene, so that the nitro group has caused an up-field shift of 0.07ppm, compared with 0.15ppm in 2,6-dimethyl-1-nitronaphthalene, if (i) is assigned as 2-methoxy-6-methyl-1-nitronaphthalene. If the alternative assignment of 2-methoxy-6-methyl-5-nitronaphthalene is given, then proton 5 has moved 0.27ppm down-field relative to proton 1 in 2-methoxy-6-methylnaphthalene. Thus it is likely that isomer(1) is 2-methoxy-6-methyl-1-nitronaphthalene, although this assignment is not unambiguous.

From spectrum(2) it is possible to pick out an AB quartet with coupling constant ca. 2c/s, characteristic of a 1-3 coupling constant. Thus the isomer is of type (ii). By comparison with the spectrum of 2,6-dimethyl-4-nitronaphthalene,(spectrum(b), ch.5), the low-field peak can be assigned to proton 5, with a shift of 1.97ppm. Now in 2,6-dimethyl-4-nitronaphthalene, proton 5 moves 0.77ppm down-field relative to 2,6-dimethylnaphthalene. Assuming that X is Me and Y is OMe in fig(ii), proton 5 moves 0.84 ppm down-field, whereas the alternative assignment would give a down-field shift of only 0.5ppm. Thus it seems reas-

Spectrum (1)



Spectrum (2)



onable to assign isomer(2) as 2-methoxy-6-methyl-8-nitronaphthalene.

From the nitrations of 2-methyl and 2-methoxynaphthalene in acetic acid/nitric acid, the following partial rate factors were obtained.[138]

	1-nitro	6-nitro	8-nitro	4-nitro	5-nitro
2-methyl	74±25	53±18	16.5±5.6	8.9±3.0	7.7±2.6
2-methoxy	10000±4000	31650±3800	1660±370		

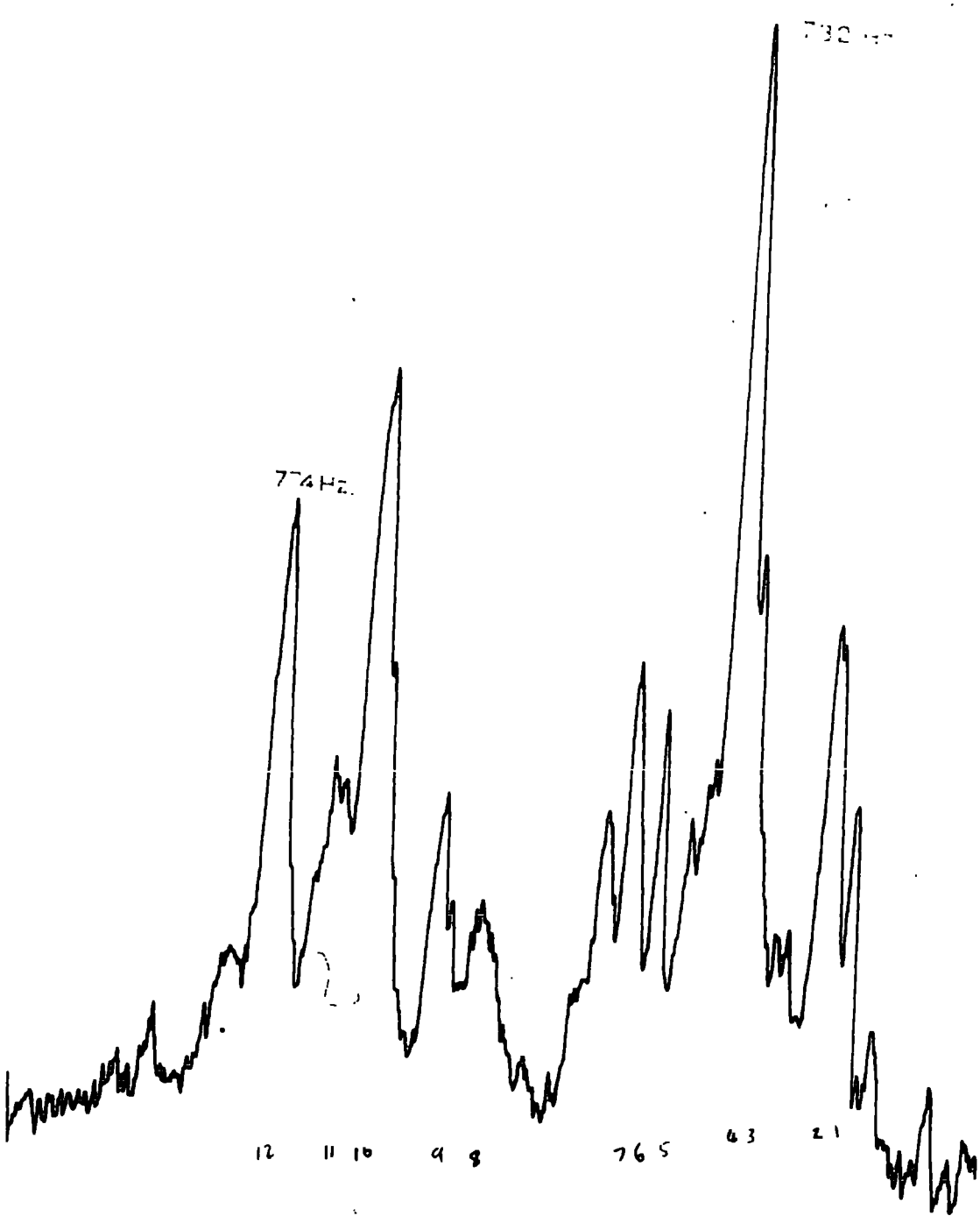
From these results it would appear certain that 2-methoxy-6-methylnaphthalene is nitrated in the order 1>8>5, in agreement with the above assignments and the fact that only 3 isomers were detected.

b) 2-Fluoro-6-Methylnaphthalene

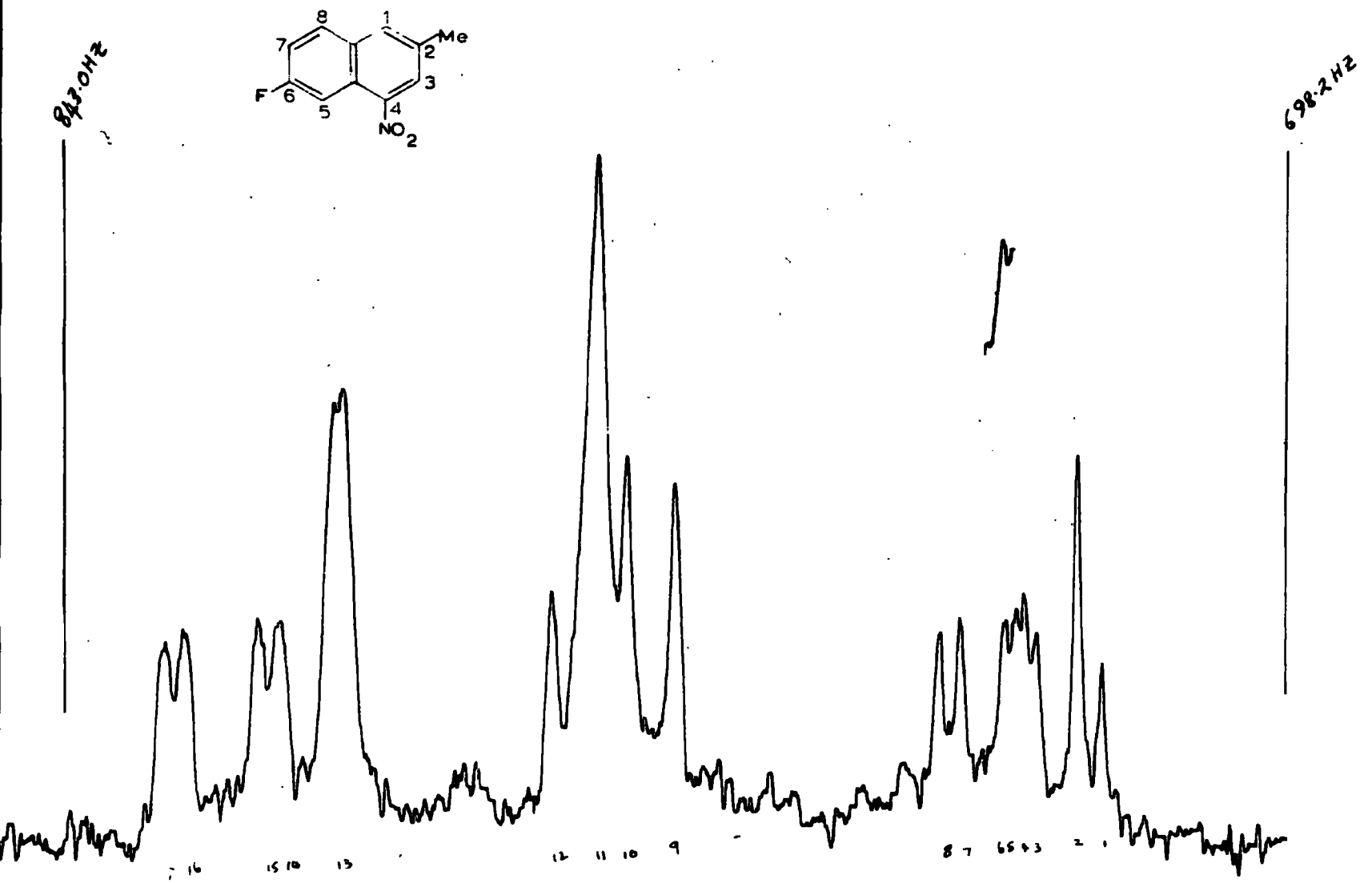
The major isomer from the nitration of 2-fluoro-6-methylnaphthalene can be assigned unambiguously as the 5-nitro derivative from its n.m.r. spectrum(3). It is possible to pick out an AB quartet (peaks 2, 4, 10 and 12) with coupling constant ca. 8c/s, characteristic of a 3-4 coupling constant. The absence of further splitting in this quartet shows that the AB system is not in the same ring as the fluorine atom.

The second isomer can be assigned unambiguously as 2-fluoro-6-methyl-8-nitronaphthalene. From the n.m.r. spectrum(4), peaks 11 and 13 form a partly resolved AB system. From the splitting of peak 13, the coupling constant can

Spectrum(3)



Spectrum(4)



be estimated as ca. 1.2c/s, characteristic of a 1-3 coupling constant. The absence of further splitting precludes the presence of the fluorine atom in the same ring as the AB system. Using the INDOR double resonance technique, the following assignment was made.[172]

Peak	Proton	Peak	Proton
1, 2, 3, 4, 5, 6, 7, 8	7	9, 10, 11, 12	8
14, 15, 16, 17	5	13; 11 (part)	1 and 3; probably 13→3

Cation localisation energies have been calculated for the above compounds, and these are given, with $\Delta\Delta E_{\pi b}$ values (relative to the appropriate naphthalene cation), in Table 3. The pi-electron density distributions were also obtained from the calculations and these are given, for the cations and neutral molecules, in Tables 4 and 5. From Table 3 it can be seen that the positional reactivities of 2-methoxy-6-methylnaphthalene are qualitatively in agreement, while 2-fluoro and 2-acetamido-6-methylnaphthalene are at variance. Now the 1-position of 2-fluoro-6-methylnaphthalene is predicted to be the most reactive, but this calculation cannot take the strong field effect of the C-F bond into account. Thus it is not surprising

Table 3 Pi-Bonding Energies of 2,6-Disubstituted Naphthalenes and their Cations.

Compound	pi-bonding energy(eV)	Cation	pi-bonding energy(eV)	$\Delta E_{\pi b}$	$\Delta E^{X}_{\pi b} - \Delta E^{naph.}_{\pi b}$
2-methoxy-6-methyl-naphthalene	-199.490	1(α)	-179.869	19.621	-2.139
		3	-178.725	20.765	-1.330
		4	-178.262	21.228	-0.532
		5(γ)	-178.806	20.684	-1.076
		7	-178.193	21.297	-0.798
		8(β)	-178.919	20.571	-1.189
2-Fluoro-6-Methyl-Naphthalene	-207.110	1	-187.253	19.867	-1.893
		3	-186.165	20.945	-1.150
		4	-185.836	21.274	-0.486
		5	-186.308	20.702	-1.058
		7	-185.760	21.350	-0.745
		8	-186.396	20.714	-1.046
2-Acetamido-6-Methyl-Naphthalene	-226.620	1	-204.852	21.768	+0.008
		3	-204.587	22.033	-0.062
		4	-205.123	21.497	-0.263
		5	-205.524	21.096	-0.664
		7	-204.897	21.723	-0.372
		8	-204.830	21.790	+0.030

Table 4

The pi-Electron Density Distributions of 2,6-Disubstituted Naphthalene Cations.

C_8	C_9	C_{10}	Me	X_1	X_2	X_3
0.9643	0.9726	1.0413	1.9588	1.9322		
0.9881	0.8633	0.9981	1.9570	1.9399		
0.8943	1.0363	0.9171	1.9416	1.9581		
0.7086	1.0328	0.9730	1.9119	1.9566		
0.7177	0.9962	0.8729	1.9307	1.9558		
	0.9100	1.0459	1.9598	1.9472		
0.9666	0.9887	1.0453	1.9592	1.8865		
0.9953	0.8634	0.9965	1.9574	1.8995		
0.8982	1.0334	0.9188	1.9422	1.9352		
0.7096	1.0284	0.9859	1.9125	1.9329		
0.7238	0.9930	0.8796	1.9312	1.9306		
	0.9056	1.0519	1.9603	1.9133		
0.9579	0.9359	1.0273	1.9582	1.8235	0.6955	1.3727
0.9652	0.8752	0.9988	1.9560	1.8401	0.6935	1.3886
0.8793	1.0405	0.9145	1.9403	1.8675	0.6887	1.4010
0.7004	1.0422	0.9422	1.9106	1.8627	0.6895	1.4053
0.6961	1.0056	0.8567	1.9294	1.8620	0.6921	1.3928
	0.9206	1.0285	1.9588	1.8497	0.6894	1.4038

Table 5

Ground State pi-Electron Density Distributions of 6-Substituted 2-Methylnaphthalenes.

C_8	C_9	C_{10}	Me	X_1	X_2	X_3
0.9994	1.0065	1.0065	1.9692	1.9692		
0.9925	1.0176	1.0007	1.9697	1.9630		
0.9867	1.0289	0.9952	1.9702	1.9443		
0.9971	1.0111	1.0042	1.9694	1.9615		
0.9856	1.0338	0.9930	1.9705	1.8977		
0.9867	1.0289	0.9952	1.9702	1.9443		
1.0080	0.9879	1.0139	1.9681	1.8580	0.7025	1.4119
1.0103	0.9731	1.0223	1.9670	0.6773	1.3797	
1.0007	1.0052	1.0073	1.9692	1.9682		
1.0033	1.0015	1.0092	1.9691	1.9621		

acetamido: X_2 = C, X_3 = O

acetyl: X_2 = O.

that the theoretical prediction is incorrect. The discrepancy between the high reactivity calculated for 2-fluoro-6-methylnaphthalene and the low substrate selectivity found experimentally is due to the use of mixed acid as nitrating agent for this compound. This nitrating agent is known to show low substrate selectivity, because of its high reactivity.[137]

The failure to predict the most reactive position of 2-acetamido-6-methylnaphthalene requires some special comment. In acetic acid media there is a possibility of an equilibrium being established, giving a small concentration of the amino compound which then undergoes nitration. This is supported by the fact that nitration of 2-acetoxy-6-methyl naphthalene under these conditions gives 2-hydroxy-6-methyl naphthalene, which is then nitrated. Another possibility is that the electrophile forms an N-nitro compound, which then rearranges under acid conditions to give the 1-nitro derivative.

For 2-methoxy-6-methylnaphthalene and 2,6-dimethylnaphthalene there should be a linear correlation between the logarithms of the partial rate factors of positions non-adjacent to substituents, and the corresponding localisation energy differences, relative to naphthalene, and figure(1) shows that this is the case. Apart from the 1-position of 2-methoxy-6-methylnaphthalene, which is adjacent to the methoxy group, the deviation from linearity is

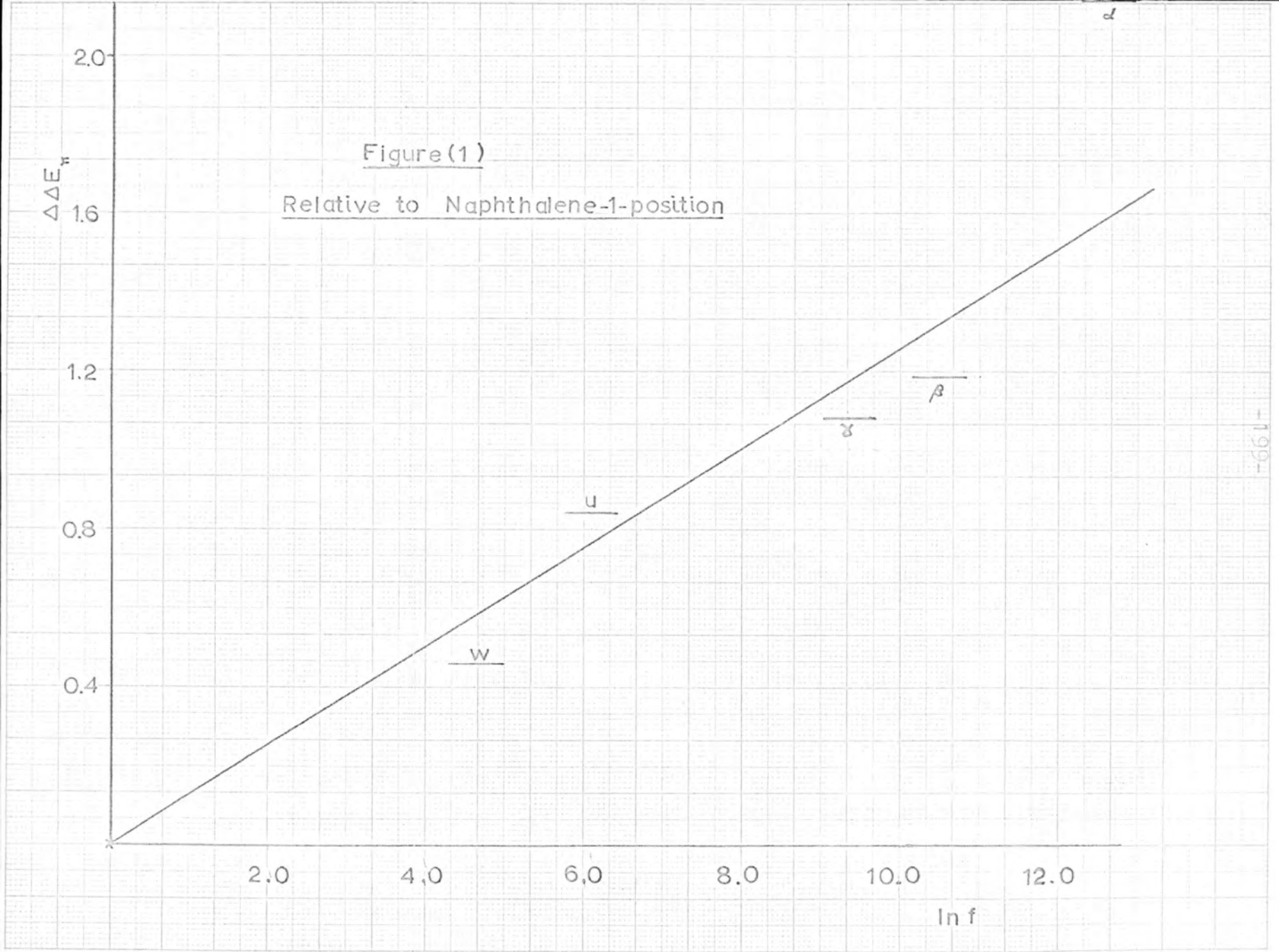


Figure (1)
Relative to Naphthalene-1-position
$\Delta\Delta E_\pi$
2.0
1.6
1.2
0.8
0.4
2.0
4.0
6.0
8.0
10.0
12.0
ln f
α
β
γ
u
w

very small.

So far in this thesis, reactivities have been discussed in terms of localisation energies. It is of interest to see whether the positional selectivities can be predicted from the ground state pi-electron distributions, given in Table 5.

a) 2,6-Dimethylnaphthalene

The most reactive site is predicted to be the 1-position, and since the electron density is >1 this should be more reactive than naphthalene, as found experimentally. However the partial rate factors expected for the 3 and 4 positions are in complete contradiction with the experimental results, since both sites are more reactive than naphthalene and the order of reactivity is 4>>3.

b) 2-Fluoro-6-Methylnaphthalene

The predicted order of reactivity is 1>3>5>7. As with the localisation energies, the 1-position is predicted to be the most reactive, however as has been indicated, the field effect is likely to be particularly adverse at this site. The order 3>5>7 emphasises the deficiency of the isolated molecule approach, since large reactivities are assigned to β positions, and the localisation energies are in much better agreement with the experimental results.

c) 2-Methoxy-6-Methylnaphthalene

The predicted order of reactivity is 1>3>5>7 as with the fluorine compound. This is to be compared with the ex-

perimental order of 1>8>5 which agrees very well with the localisation energy calculations.

d) 2-Acetamido-6-Methylnaphthalene

As with the localisation energy calculations, the 5-position is predicted to be the most reactive, so that neither method correctly predicts the most reactive position of this molecule.

3. Experimental

a) 2-Methoxy-6-Methylnaphthalene

2-Methoxy-6-methylnaphthalene(0.86g, 5mmole) and 2,6-dimethylnaphthalene(0.78g, 5mmole) were dissolved in glacial acetic acid(20ml) and allowed to equilibrate at 25°, before treating with a solution of nitric acid(0.32g, 5 mmole) in acetic acid(1ml), prepared as described in ch.5. The solution was stirred ca. 1200rpm for 5hr. before quenching and extracting as described in ch.5. The extracted product was shown by glc analysis to contain 3 nitro isomers of 2-methoxy-6-methylnaphthalene in approximate proportions 20:2:1.

2-Methoxy-6-methylnaphthalene(5g) was nitrated at 100° for 5hr. with nitric/acetic acid, in order to obtain a separable amount of the nitro derivatives, using the same procedure as for the analytical runs. The reaction product was eluted down a 12x1 in. alumina column (Camag, Brockmann activity 1), using carbon tetrachloride as eluent. Two fractions were collected; one of these was shown by

glc analysis to contain ca. 90% of the major isomer (1), while the second fraction contained ca. 80% of isomer (2) and 10% of each of isomers (1) and (3). Fraction (1) was eluted on a thick-layer plate (Kieselgel) using a 1:10 v/v mixture of chloroform and carbon tetrachloride as eluent. One fraction was obtained which sublimed at 70° (0.001mm) to give a yellow solid, m.p. 106-107°. (Found: C,66.24; H, 4.86; calc. for $C_{12}H_{11}NO_3$: C,66.3; H,5.1%). The 100 Mc/s n.m.r. spectrum obtained using a Varian HA-100 spectrometer (spectrum(1), sweep width 250 c/s) was in agreement with the isomer being 2-methoxy-6-methyl-1-nitronaphthalene. Elution of fraction (2) enabled a separation of isomers (2) and (3) from (1), but none of the many eluents used would completely separate (2) and (3). Glc analysis showed the ratio of the isomers in the final fraction obtained to be 6:1. Spectrum(2) is the 100Mc/s n.m.r. spectrum of this mixture (sweep width 250 c/s), from which isomer(2) was deduced to be 2-methoxy-6-methyl-8-nitronaphthalene. As already discussed, it appeared reasonable to assign isomer (3) as the 5-nitro derivative.

b) 2-Acetamido-6-Methylnaphthalene

A competitive nitration was carried out between 2-acetamido-6-methylnaphthalene and naphthalene at 25° in acetic acid, using the previously described procedure. Glc analysis of the product showed only one nitro isomer of 2-acetamido-6-methylnaphthalene. The product obtained from

a preparative scale nitration (0.5g), using the conditions of the analytical runs, was hydrolysed by refluxing for 2hr. in 50% v/v aqueous sulphuric acid(10ml) and ethanol(10ml). Excess of ammonium hydroxide was added, and the precipitated amine filtered, washed, and dried in vacuum.(50°, 0.001mm) Crystallisation from benzene gave 2-amino 6-methyl-1-nitronaphthalene, m.p.165-167°(lit.[167] 166-167°).

c) 2-Fluoro-6-Methylnaphthalene

2-Fluoro-6-methylnaphthalene gave a complex mixture of isomers on nitration with nitric/acetic acid at 25°. It was not possible to separate the mixture and a competitive run under these conditions could not have been successfully analysed. The following procedure gave a much simpler reaction product, which could be separated and analysed.

2-Fluoro-6-methylnaphthalene(0.8g, 5mmole) and naphthalene(0.64g, 5mmole) were dissolved in acetic acid(20ml) and allowed to equilibrate at 25°. The solution was treated, while stirring ca.1200 rpm, with a 30% w/w solution of nitric acid(0.3g, 5mmole) and sulphuric acid(0.5g, 5mmole) in acetic acid. After 12hr., the reaction mixture was extracted as described in ch.5. Glc analysis showed the presence of 3 isomers of 2-fluoro-6-methylnaphthalene in approximate proportions 6:3:1. A preparative scale nitration was carried out using 30% mixed acid in acetic acid, nitrating at 60° for 12hr. Thick-layer chromatography of the extracted product, using 1:2 v/v cyclohexane:carbon tetra-

chloride as eluent, gave only two fractions which could not be further separated. Fraction(1) sublimed at 110° (15mm) as pale yellow needles, m.p. 62-63°. (Found: C, 64.7; H, 4.16; calc. for $C_{11}H_8NO_2F$: C, 64.4; H, 3.9%) The glc retention time corresponded to the major isomer of the competitive nitration, and the 100Mc/s n.m.r. spectrum(3) showed unambiguously that the isomer was 2-fluoro-6-methyl-5-nitronaphthalene. Fraction (2) sublimed at 110° (12mm) as long yellow needles, m.p. 118.5-119.5°. (Found: C, 64.0; H, 4.2%). The glc retention time corresponded to the second largest peak of the competitive nitration, and the 100Mc/s n.m.r. spectrum(4) showed unambiguously that the isomer was 2-fluoro-6-methyl-8-nitronaphthalene. The third isomer would probably be the 1-nitro derivative, but it was impossible to obtain a sample for confirmation.

All of the competitive nitrations described above were analysed by gas-liquid chromatography as described in ch. 5, the glc traces being calibrated using standard solutions of the appropriate nitro compounds. Three runs were carried out for each mixture, the errors being estimated from the mean of a minimum of two chromatographic analyses of each run.

CHAPTER 9

Nuclear Magnetic Resonance. A Discussion of the Correlation between Chemical Shifts and Calculated pi Electron Densities.

1. Introduction

In principle, chemical shifts provide direct measures of local electronic and magnetic environments of individual atoms in molecules. The shielding of a nucleus is very sensitive to changes in the electronic environment of the molecule as a whole and, in many cases, can not be related to the electron density about that molecule alone. If the comparison of the shielding parameters is confined to a series of closely related compounds in which the contributions to the shielding from factors other than the variation in electron density may be reasonably constant, this difficulty may be overcome.

2. N.M.R. Spectra of Substituted Benzenes.

There are strong grounds for believing that chemical shifts, relative to benzene, of both ^{1}H and ^{13}C nuclei para to the substituent are directly proportional to the change in pi electron density at the para carbon atom, thus:[183]

$$\delta_{H} = k_{1_H} \Delta P_{CC} \qquad (1)$$

$$\delta_{^{13}C} = k_{^{13}C} \Delta P_{CC} \qquad (2)$$

where the two constants can be found empirically by comparing the shifts of ^{1}H and ^{13}C nuclei in cyclopentadienyl anion, benzene, tropylium cation, and cyclo-octatetraene dianion.[183,184] The value of k_H depends on the model chosen

for the ring currents in these molecules, but almost certainly lies between 8.00 and 10.6 p.p.m./electron.[183-185] The value of $k_{^{13}C}$ has been estimated as 160 p.p.m./electron. Using $k_{^{1}H}$ = 8.00 ppm/electron and $k_{^{13}C}$ = 160 ppm/electron, chemical shifts have been calculated relative to benzene using the following models:

a) mesomeric only

b) mesomeric + σ-inductive

c) mesomeric + σ and π-inductive

d) π-inductive only.

The results are shown in table 1.

Compound	Method	Chemical shifts in p.p.m. relative to benzene				Reference
			^{1}H	^{13}C		
		Calc.	obs.	Calc.	obs.	
C_6H_5F	a	0.09		1.74		5
	b	-0.08		-1.42		5
	c	0.31	0.22	6.10	4.4	5, 171
C_6H_5Cl	a	0.10		1.98		5
	c	0.23	0.22	4.64	2.0	5, 196
$C_6H_5NH_2$	a	0.08		1.60		5
	c	0.53	0.62	10.56	9.5	5, 171
C_6H_5OH	a	0.12		2.30		5
	c	0.46	0.48	9.17	6.1	187, 188
$C_6H_5CH_3$	d	0.09		1.62		This work
	a	0.11		1.79		This work
	c	0.20	0.18	3.45	3.05	186

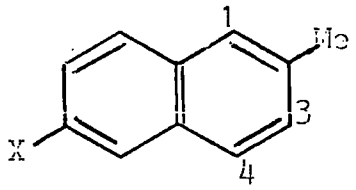
Table 1 Calculated and observed ^{1}H and ^{13}C chemical shifts.

(Positive shifts indicate greater screening than in benzene)

It can be seen that the calculations(a) which do not include σ or π-inductive effects, underestimate chemical shifts. Similarly with the model including the π-inductive effect but no mesomeric effect. Including only a σ-inductive effect for fluorobenzene (b) gives ^{1}H and ^{13}C chemical shifts opposite in sign to those observed. However the correct magnitude and sign is given for all compounds when method (c) is used. Thus the best model for calculating charge densities is one including mesomeric and σ and π-inductive effects.

3. Proton N.M.R. Spectra of 6-Substituted 2-Methyl-Naphthalenes.

Initially it was hoped that in a system such as 2,6-disubstituted naphthalenes, where one of the substituents was retained as methyl while the other was varied, the major change in contribution to the proton shielding constants would arise from changes in pi electron density at the adjacent carbon atoms, (which are directly calculable), and that the effects such as the diamagnetic anisotropy of the X group would be minimised. Also, since the n.m.r. spectra of these compounds should consist of two overlapping ABC systems, it was hoped that the analysis of the ^{1}H spectra for a series of compounds would not prove too difficult. In fact this was not the case, and for most of the compounds 220Mc/s spectra were



required to obtain an initial set of spectral parameters. Spectra (1)-(5) show the low-field aromatic regions of the 100Mc/s n.m.r. spectra of some of these compounds. (Run on an HA-100 spectrometer with a sweep width of 1000 c/s.)

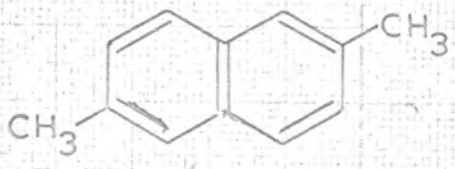
The parameters obtained from the 220Mc/s spectra were used to generate a trial 100Mc/s spectrum by computer. INDOR experiments showed unambiguously the relative signs of the coupling constants involved and the lines associated with each ABC system.[172] The experimental peaks were then assigned to the calculated energy level differences and an iterative computer programmed process was used to give the final set of chemical shifts and coupling constants.[172]

The compounds studied were 6-substituted 2-methylnaphthalene compounds where the substituent was methyl, fluorine, chlorine, bromine, iodine, NO_2, OH, OMe, COMe and NHCOMe. Ideally one would like the spectral parameters for the molecules in a solvent in which strong solvent interactions were absent. This requirement is usually met by studying dilute solutions of the compounds in carbon tetrachloride. Unfortunately, the hydroxy, methoxy, fluoro and acetamido compounds were insufficiently soluble in this solvent, so that the spectra were recorded with acetone as solvent.

Results

Table 2 shows the chemical shifts (in c/s downfield

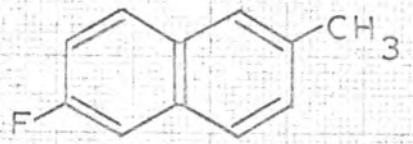
(1)

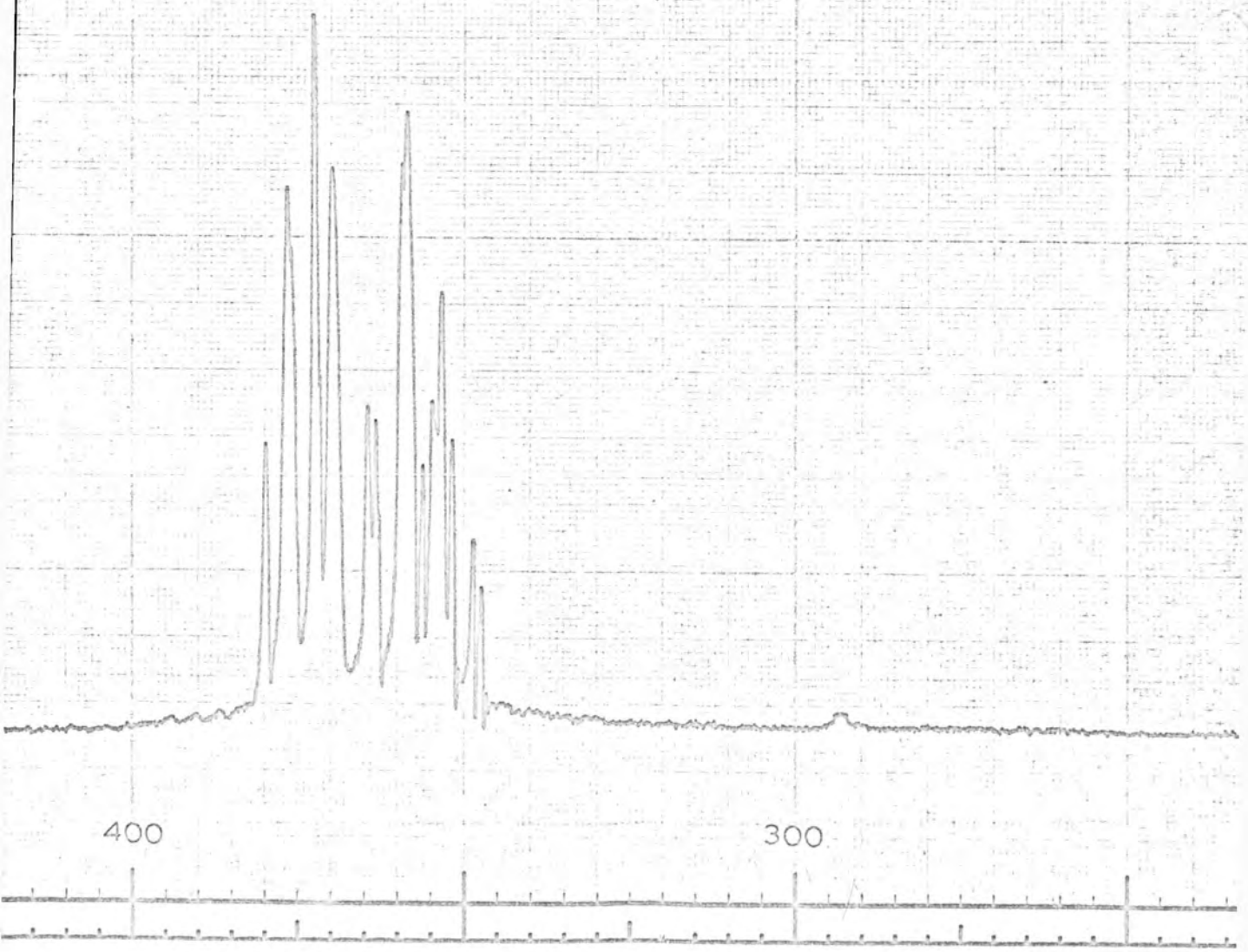


400

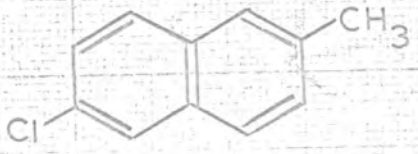
300

(2)





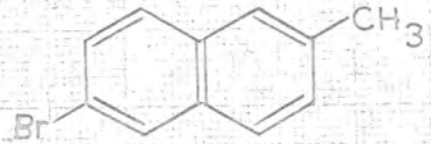
(3)



400

300

(4)



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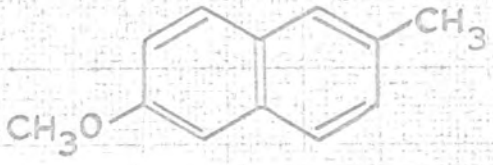
(5)



400

300

Table 2

Chemical Shifts and Coupling Constants of 6-Substituted 2-Methylnaphthalenes at 100Mc/s.

X	Chemical shifts (c/s from TMS at 100Mc/s)						J_{HH} (c/s)				
In CCl_4	H_1	H_3	H_4	H_5	H_7	H_8	1-3	3-4	5-7	7-8	
Me	744.0	715.6	751.8	744.0	715.6	751.8		8.2		8.2	
Cl	746.6	720.6	756.0	767.3	729.6	753.6	1.9	6.6	1.75	7.5	
Br	749.1	721.3	756.2	787.8	744.8	751.3	1.5	8.4	1.7	8.8	
I	746.6	722.6	752.6	809.1	759.0	738.6	1.95	8.3	1.6	8.6	
NO_2	763.0	738.5	784.8	865.4	815.1	776.6	1.75	8.7	2.2	9.1	
SO_2Cl	790.2	764.0	817.0	821.1	801.8	818.9		8.6	2.0	9.0	
acetone											
OH	758.8	728.8	762.2	718.2	715.8	770.7	2.0	8.5	2.6	8.2	
OMe	753.2	723.9	764.1	718.8	707.2	764.7	1.9	9.6	2.6	8.6	
COMe	780.0	751.1	803.8	862.2	805.9	792.9	1.5	8.4	1.7	8.5	
F*	757.8	736.9	792.4	776.3	746.2	785.5	2.6	8.7		8.5	*J_{FH}^{ortho} = 8.7
NHCOMe	761.4	734.4	773.6	836.2	773.1	765.7	1.7	8.2	2.2	8.9	*J_{FH}^{meta} = 5.5

from TMS) and coupling constants obtained from the analysis of the 100Mc/s spectra.

Discussion

It is somewhat unfortunate that some of the compounds were studied in acetone solution, since this makes direct comparison of the chemical shifts of these compounds with the shifts of the compounds studied in carbon tetrachloride solutions rather difficult.

Considering first the results for the compounds in carbon tetrachloride solutions, these are given in Table 3.

Table 3

X	Chemical Shifts			Electron Densities		
	H_1	H_3	H_4	C_1	C_3	C_4
Me	744.0	715.6	751.8	1.0552	1.0344	0.9994
Cl	746.6	720.6	756.0	1.0547	1.0343	1.0013
Br	749.1	721.3	756.2	1.0554	1.0348	0.9989
I	746.6	722.6	752.6	1.0559	1.0352	0.9977
F*	757.3	736.9	792.4	1.0539	1.0335	1.0038

For X= NO_2, the self-consistent field calculation failed to converge after 20 iterations, so that no results could be obtained. For X = SO_2Cl, no inductive parameters were available, so that a calculation could not be attempted.

The changes in electron density at each position, on replacement of Me by halogen, are very small, and this is

in good agreement with the small range spanned bt the chemical shifts. If the fluorine compound is included (although the magnitude of the solvent effect is uncertain), the shifts at the 1 and 3 positions are qualitatively in the direction expected from the relatively large change in electron densities at these positions, on replacement of Me by F. At the 4 position, the relatively large downfield shift on replacement of Me by F is at variance with the increase in electron density at this position, but this could be due to the field effect of the C-F bond, which is relatively close to the 4 position.

The results for the compounds studied in acetone solutions are given in Table 4.

Table 4

X	Chemical Shifts			Electron Densities		
	H_1	H_3	H_4	C_1	C_3	C_4
OH	758.8	728.8	762.2	1.0527	1.0331	1.0086
OMe	753.2	723.9	764.1	1.0527	1.0331	1.0086
COMe	780.0	751.1	803.8	1.0571	1.0321	0.9828
F	757.8	736.9	792.4	1.0539	1.0335	1.0038
NHCOMe	761.4	734.4	773.6	1.0587	1.0337	0.9854

The use of acetone as solvent, in which specific associations might lead to substantial solvent shifts, makes it difficult to interpret these results in any simple fashion.

For the compounds containing carbonyl groups, the shifts are qualitatively in agreement with the change in pi electron density at all three positions. However thet disagree with the results for the hydroxy, methoxy and fluoro substituted compounds. At positions 1 and 3, the chemical shifts are very similar for these three compounds and this in agreement with the pi electron densities. At position 4 the fluoro compound has a downfield shift relative to the other two compounds and this is consistent with the decrease in electron density at carbon 4, on replacement of OH or OMe by F.

In all these compounds, the changes in pi electron density are in the third and fourth places of decimals. It would be optimistic to expect the calculations to show this degree of agreement with experiment, so that the correspondences between experimental and theory that have been found are really quite good. Thus one can conclude that the inductive-mesomeric model that has been used throughout this thesis gives good agreement with all the experimental ground and excited state properties studied.

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